EVALUATION OF DIFFERENT SURFACTANT-POLYMER SYSTEMS FOR EOR APPLICATIONS IN HIGH-TEMPERATURE HIGH-SALINITY SAUDI CARBONATE RESERVOIRS

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BY

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DEDICATION

Dedicated to my beloved parents

Mr. & Mrs. Kamal Din

Dedicated to my wife, brothers and sister

Dedicated to my friends and those who love me more than anything

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ABSTRACT

Full Name : MUHAMMAD SHAHZAD KAMAL

Thesis Title : EVALUATION OF DIFFERENT SURFACTANT-POLYMER SYSTEMS FOR EOR APPLICATIONS IN HIGH-TEMPERATURE HIGH-SALINITY SAUDI CARBONATE RESERVOIRS

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Only one third of oil can be recovered from oil fields using conventional primary and secondary recovery techniques. To recover major fraction of the remaining oil, enhanced oil recovery (EOR) methods are required. Chemical EOR is a technique to recover additional oil using surfactant, polymer and/or alkali. In this study, interactions between different surfactants and polymers were investigated at high-temperature and high-salinity for EOR in carbonate reservoirs. Comprehensive experimental approach was adopted to investigate performance of different surfactants and polymers using thermal stability, rheology, phase behavior, adsorption and interfacial tension measurements. Major parameters covered in this study were: polymer type and concentration, surfactant type and concentration, temperature and salt concentration. Oil recovery experiment was performed in carbonate core for best surfactant-polymer system. A mesoscale simulation method, dissipative particle dynamics was used to model interfacial tension between oil and water. Thermoviscosifying polymers showed most promising results at high-temperature and high-salinity conditions. Contrary to other polymers, the thermoviscosifying polymer showed increase in the viscosity with increase in temperature. The amphoteric surfactant showed better compatibility, lower adsorption on carbonate rock and better efficiency in lowering oil water interfacial tension. About 22% additional oil recovery was obtained using surfactant-polymer system consisting of amphoteric surfactant and thermoviscosifying polymer at 90^{o}C.

ملخص الرسالة

الاسم الكامل: محمد شهزاد كمال

عنوان الرسالة: تقييم أداء خوافض التوتر السطحي و البوليمرات عند إستخدامها في عمليات تعزيز إستخراج النفط عند درجات حرارة عالية و تركيز أملاح عالي في أبار النفط الكربونية بالمملكة العربية السعودية.

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ديسمبر 2014

تقدر كميات النفط المستخرجة بواسطة عمليات إستخراج النفط الأولية حوالي الثلث. و لإستخراج الكميات المتبقة من النفط الخام يتم إستخدام تقنيات إستخراج النفط المعزز. أحد هذه التقنيات يتم فيها إستخدام المواد الكيميائية كالبوليمرات و خوافض التوتر السطحي. تم في هذه الدراسة تقييم عدة بوليمرات و خوافض توتر سطحي عند درجات حرارة عالية و درجات ملوحة عالية للإستخدام في أبار النفط الكربونية. حيث تم إعتماد منهج تجريبي شامل لتقييم الاداء كدراسة الإستقرار الحراري و الخواص الريولوجية و الإدمصاص و طاقة التوتر السطحي بين الماء و النفط. تم كذلك دراسة تأثير عدة عوامل خلال إجراء التجارب كنوع و تركيز البوليمر, نوع و تركيز خافض التوتر السطحي, درجة الحرارة و تركيز الأملاح. و لتقييم مدى كفاءة المواد الكيميائية في عمليات إستخلاص النفط, تم إستخراج النفط من تكوين الكربونات عن طريق الضخ خلالها. بالاضافة الى ذلك, تم محاكاة قياس طاقة التوتر السطحي بين الماء و النفط بواسطة إستخدام نموذج ديناميات الجسيمات المبددة. تم التوصل خلال هذه الدراسة الى أن الثيرموفيسكوفاينج بوليمر يظهر نتائج واعدة عند درجات حرارة عالية و تركيز املاح مرتفع. حيث لوحظ إرتفاع لزوجته عند زيادة درجة الحرارة. لوحظ كذلك أن خافض التوتر السطحي المتذبذب الشحنة يظهر توافقية افضل و إدمصاص أقل مقارنة بغيره. كذلك أظهر مقدرته على خفض طاقة التوتر السطحي بين الماء و النفط. أظهر خليط خافض التوتر السطحي المتذبذب الشحنة و الثيرموفيسكوفاينج بوليمر زيادة في عملية إستخراج النفط قدرت بحوالي 22 % عند درجة حرارة تبلغ 90 درجة مئوية.

CHAPTER 1

INTRODUCTION

1.1 Chemical Enhanced Oil Recovery

About 2,000 billion barrels of conventional oil and 5,000 billion barrels of heavy oil will remain in the reservoirs after applying conventional oil recovery methods like water flooding (Thomas 2007; Wu, Mahmoudkhani et al. 2012). To recover this major fraction of the remaining oil, enhanced oil recovery (EOR) methods are required (George and Zhang ; Wyatt, Pitts et al. ; Yeow Chong, Bakar et al. ; Zhang and Kang ; Zhou, Zhang et al. ; Koning, Mentzer et al. 1988; Van Wunnik, Stoll et al. 2014). Many considerations like oil and rock properties, economic feasibility, technology and availability of raw materials decide the suitable EOR method for a particular reservoir. Chemical EOR (cEOR), thermal EOR and gas flooding are the most popular EOR methods used for recovering additional oil under different reservoir conditions. In cEOR, surfactant polymer, alkali or a combination of these chemicals is used. The surfactant reduces the interfacial tension (IFT) between oil and water while the polymer modifies the rheology of flooding water by increasing its viscosity. Alkalis are used for adjusting the pH to minimize surfactant's adsorption. Alkalis also react with oil, leading to in situ generation of surfactants.

Water soluble partially hydrolyzed polyacrylamide (HPAM) is widely used in cEOR applications. HPAM is the first choice among the available water soluble polymers for cEOR applications due to many desirable properties such as large hydrodynamic volume in water and easy to form hydrogen bond with water molecules (Wu, Mahmoudkhani et al. 2012). HPAM works well in low-salinity low-temperature reservoirs but it is highly unsuitable for high-temperature high-salinity (HTHS) environments (Sabhapondit, Borthakur et al. 2003; Levitt, Jackson et al. 2006; Levitt and Pope 2008). HPAM chain is highly flexible and at HTHS it starts folding resulting in a huge decrease in the viscosity. Polymer interactions with salts and surfactant at high salinity may cause phase separation. Hydrolysis at high temperature may occur and interaction of the hydrolyzed products with divalent cations will lead to polymer's precipitation (Moawad, Elhomadhi et al. 2007; Wang, Feng et al. 2010; Kulawardana, Koh et al. 2012). Replacing some of the acrylate monomer by other monomers showing lower sensitivity to cation shielding, shear and chemical alteration can enhance the thermal stability of the polymer. Surfactants are the second important component of SP flooding. Different surfactants have been synthesized for cEOR applications but at HTHS surfactants may degrade or phase separation may occur. Due to these problems, HTHS reservoirs are still a big challenge for cEOR.

Most of Saudi Arabian oil reservoirs have HTHS conditions with fractured carbonate reservoir. Therefore, classical HPAM is not suitable for these reservoirs having temperature > 80^{o}C. Main objective of the study was to identify potential surfactant-polymer formulations for Saudi carbonate reservoir. This will be achieved using systematic experimental approach which includes: rheology, thermal stability, phase

behavior, adsorption, interfacial tension measurement and core flooding. Mesoscale simulation technique dissipative particle dynamics will be utilized to model oil/water IFT.

1.2 Thesis Summary

This section will highlight main outline of this manuscript-based

Chapter 2

In this chapter, water soluble polymers used for chemical enhanced oil recovery are reviewed. Conventional and novel modified polymers are discussed along with their limitations. The review covers thermal stability, rheology, and adsorption behavior of various polymer systems in sandstone and carbonate reservoirs. Field and laboratory core flooding data of several polymers are covered. The review describes the polymer systems that are successfully applied in low-temperature and low-salinity reservoirs. Comprehensive review of current research activities aiming at extending polymer flooding to high-temperature and high-salinity reservoirs is performed. The review has identified current and future challenges of polymer flooding

Chapter 3

In this chapter, a SP system consists of a copolymer of acrylamide (AM) and acrylamido tertiary butyl sulfonate (ATBS) and sodium dodecyl sulphate (SDS) surfactant was evaluated. Effects of surfactant concentration, temperature, polymer concentration and salinity on rheological properties of SP system were investigated by using both dynamic and steady shear measurements. Comparison with classical HPAM was made. For the

same temperature range, the viscosity drop for HPAM was about four times higher than the viscosity drop for ATBS-AM copolymer. In salt-free water, viscosity of both polymers and SP system was very high as compared to viscosity in saline water. The addition of 0.1 % surfactant to the polymer resulted in a 60% decrease in the viscosity. Addition of 0.1 % surfactant showed a 65% decrease in G′ at SP solution-oil interface. SP system consisting of ATBS-AM and SDS showed better performance at high temperature compared to the previously reported HPAM-SDS system. Due to precipitation, the SP system should be restricted to environment having low divalent cations.

Chapter 4

Thermal stability and rheological properties of a novel surfactant-polymer system containing non-ionic ethoxylated fluorocarbon surfactant was evaluated. A copolymer of AM and ATBS was used. Thermal stability and surfactant structural changes after aging at 100^{o}C were evaluated using TGA, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and FTIR. The surfactant was compatible with AM-AMPS copolymer and synthetic sea water. No precipitation of surfactant was observed in sea water. The surfactant was found to be thermally stable at 100^{o}C and no structural changes were detected after exposure to this temperature. At low temperature (50^{o}C), the viscosity initially increased slightly with the addition of the surfactant, then decreased at high surfactant concentration. At high temperature (90^{o}C), the increase in the viscosity with the increase in surfactant concentration was not observed. Overall, the influence of the fluorocarbon surfactant on the viscosity of SP system was weak particularly at high temperature and high shear rate. Salts present in sea water reduced the viscosity of the polymer due to charge shielding effect. However, the surfactant was found to be thermally stable in the presence of salts.

Chapter 5

The rheological properties of the TVP-fluorocarbon surfactant and their interactions with different salts are studied. The effects of surfactant concentration, polymer concentration, salinity and different inorganic salts on the rheological properties of the TVP and the surfactant-polymer (SP) system are evaluated. Critical association temperature (T_{cass}) is found to be a function of the TVP concentration and salinity. At low salinity, only thermo-thinning behavior is observed in the entire temperature range. At high salinity, thermo-thinning is obtained in the low temperature range ($<T_{cass}$) followed by thermo-thickening at high temperatures ($>T_{cass}$). The interfacial tension between the crude oil and the TVP solution is reduced by 3 orders of magnitude using a combination of the fluorocarbon surfactant and the co-surfactant. About 22% additional oil recovery is obtained using the TVP and the SP injection. The TVP showed much better performance and promising results at HTHS conditions compared with commercially available HPAM. At HTHS conditions, HPAM suffers huge viscosity loss due to thermo-thinning and charge screening. On the other hand, the high viscosity of the TVP due to thermo-thickening increases the oil recovery at HTHS conditions. The thermo-thickening tendency is enhanced in presence of salts that make it more promising for EOR.

Chapter 6

In this chapter carboxyl betaine based amphoteric and propoxylated anionic surfactants were evaluated for potential application in cEOR. Thermal stability of the surfactants was assessed using a novel approach based on FTIR, NMR and TGA analyses. The anionic surfactant showed lower initial IFT compared to the amphoteric surfactant. After aging at

90^{o}C for a period of 10 days, the amphoteric surfactant maintained its IFT, while almost two orders of magnitude increase in the IFT of the anionic surfactant was observed. TGA analysis showed that the two surfactants were thermally stable for short exposure times. For long term stability, both FTIR and NMR analyses showed structural changes in the aliphatic region after aging in the anionic surfactant. The thermally stable amphoteric surfactant was further evaluated at different concentrations, temperatures and salinity. By increasing the surfactant concentration, IFT decreased initially and then increased with the increase in surfactant concentration. The oil /water IFT decreased by adding salts and increased with the increase in temperature. The results of NMR, FTIR and TGA techniques showed good correlation with IFT measurements and showed the potential of using these techniques in screening surfactant.

Chapter 7

A mesoscale simulation technique dissipative particle dynamics (DPD) was used to model the oil water interfacial tension in presence and absence of surfactant. Different model compounds with varying number of hydrocarbon chain were selected which include: hexane, nonane, dodecane and pentadecane. Interfacial density, interfacial thickness and interfacial tension was investigated by varying the simulation time, no of molecules, chain branching and surfactant concentration. Well defined oil/water interface was observed. Interfacial tension increased with increasing simulation steps and finally achieves a plateau. By increasing hydrocarbon tail interfacial tension was found to be increased. Simulation results for oil water system were in good quantitative and qualitative agreement with experimental results. Sodium dodecyl sulphate surfactant was also simulated at oil water interface. Simulation results suggest decrease in interfacial

tension by increasing surfactant molecule similar to experimental observations. DPD technique can be applied for ternary system of oil, water and surfactant with reasonable success.

Chapter 8

Brief summary of the conclusion and recommendations will be presented in this chapter

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CHAPTER 2

REVIEW ON POLYMER FLOODING: RHEOLOGY, ADSORPTION, STABILITY AND FIELD APPLICATIONS OF VARIOUS POLYMER SYSTEMS

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Abstract

Polymer flooding is one of the most promising techniques for the recovery of residual oil from oil reservoirs. Water soluble polymers are used to enhance the viscosity of displacing fluid and to improve the sweep efficiency. In this paper, water soluble polymers used for chemical enhanced oil recovery are reviewed. Conventional and novel modified polymers are discussed along with their limitations. The review covers thermal stability, rheology, and adsorption behavior of various polymer systems in sandstone and carbonate reservoirs. Field and laboratory core flooding data of several polymers are covered. The review describes the polymer systems that are successfully applied in low-temperature and low-salinity reservoirs. Comprehensive review of current research activities aiming at extending polymer flooding to high-temperature and high-salinity reservoirs is performed. The review has identified current and future challenges of polymer flooding.

Keywords: polymer flooding; enhanced oil recovery; rheology; thermal stability; adsorption

2.1 Introduction

The demand for oil is growing and it is expected that oil will be the biggest contributor to world energy needs for at least the next two decades (Al Adasani and Bai 2011). To meet the ever increasing demand of energy, it is extremely important to recover the maximum amount of oil from all producing reservoirs along with the exploration of new fields. It is estimated that about 70% of the oil is left behind in a reservoir if only the conventional oil recovery methods are employed (Yang, Wang et al. 2004; Kang, Zhang et al. 2011). Enhanced oil recovery (EOR) methods are therefore deemed inevitable for application in most oil fields to recover this major fraction of unrecovered oil. Chemical EOR (cEOR) is one of the promising EOR methods in which surfactants (S), polymers (P) and/or alkali (A) are used. Polymers enhance the viscosity of displacing fluid and decrease the water/oil mobility ratio (Buchgraber, Clemens et al.). Reduction in the mobility ratio leads to an increase in the macroscopic displacement efficiency (Pancharoen, Thiele et al. ; Zerpa, Queipo et al. 2005). Recently, it was discovered that the viscoelastic nature of the polymers also helps in increasing the microscopic efficiency (Wang, Xia et al. 2001; Petit, Karakasyan et al. 2007; Zhang and Yue 2008; Masalmeh, Ligthelm et al. 2014).

A chemical EOR method which makes use of polymers is termed polymer flooding (PF). Polymer flooding has been deployed in the field for about 40 years (Mogollon and Lokhandwala 2013). The common expectation from the use of PF is to obtain 50% ultimate recovery with 15 to 20% incremental recovery over water flooding (Algharaib, Alajmi et al. ; Algharaib, Alajmi et al. 2014). Water cut can be reduced up to 50% and the resistance factor can be increased by 5 to 15% as a result of polymer flooding (Mogollon

and Lokhandwala 2013). China is leading in the implementation of PF projects (Manrique, Thomas et al. ; Saleh, Wei et al. 2014) and Daqing oil field of China is the largest oil field in terms of PF project deployment (Demin, Jiecheng et al. 2000). Up to 2004 there were 31 commercial scale PF projects only in the Daqing field with 2427 injection wells. Oil production using PF has reached about 73.5 million barrels, approximately 23% of the total oil production (Chang, Zhang et al. 2006)**.** In 2013, more than 200 million stock tank barrels of incremental oil were recovered by PF in Daqing. In USA, polymer flooding was on its peak in mid 1980s and has experienced a drastic decrease in the last three decades. In Europe, Germany and Austria have plans to start polymer flooding(Manrique, Muci et al.). In Middle East, only Oman has applied PF in the Marmul field (Al-Mutairi and Kokal) and cEOR implementation is in progress in the Sabiriyah Maudded oil field in North Kuwait(Al-Saad, Tiwari et al.). It is expected that first EOR from this carbonate reservoir will be obtained in 2016 (Al-Saad, Tiwari et al.).

Large number of polymers is available commercially for cEOR applications. Partially hydrolyzed polyacrylamide (HPAM) is one of the most widely used polymers in polymer flooding. There are some review reports available on water soluble polymers for cEOR applications (Morgan and McCormick 1990; Taylor and Nasr-El-Din 1998; Wever, Picchioni et al. 2011). Taylor et al. (Taylor and Nasr-El-Din 1998) reviewed hydrophobically associating polymers for improved oil recovery. Their main focus was to the synthesis and characterization. Weaver et al. (Wever, Picchioni et al. 2011) focused on rheological properties of water soluble polymers. In this review, the thermal stability limits, adsorption in sandstone and carbonate rocks, rheology, core flooding results, and field implementation of various water soluble polymers is reviewed. In addition, recent

advances in HPAM modification for severe conditions of salinity and temperature are covered.

2.2 Potential Polymer Systems for cEOR

2.2.1 Polyacrylamide

Polyacrylamide (PAM), the structure of which is shown in Figure 2-1, is non-ionic in nature in the un-hydrolyzed form. Non-ionic PAM is not used for EOR applications due to its high adsorption on mineral surfaces (Sheng 2010). However, most of the currently used cEOR polymers are modified forms of PAM, which are discussed in the following sections.

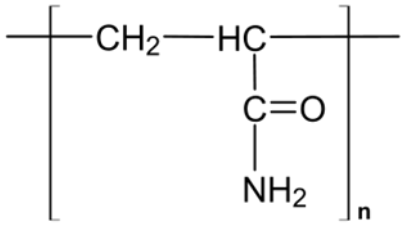

Figure 2-1**:** Structure of PAM

Although PAM does not hydrolyze at room temperature (Kurenkov, Hartan et al. 2001), the pendant amide group present in PAM may undergo hydrolysis at elevated temperature and/or pH. Hydrolysis of PAM was observed by Muller in 1980. Changes in the viscosity and pH of an aged sample were observed at high temperature (Muller, Fenyo et al. 1980; Muller 1981; Muller 1981).The hydrolysis results in the formation of a carboxylate group making the backbone negatively charged. The negative charge on the backbone enhances the viscosity due to intermolecular repulsion (Xu, Gao et al. 2011). PAM is normally post hydrolyzed by the addition of alkali, forming partially hydrolyzed PAM, for EOR

applications. Partially hydrolyzed PAM or its salts can be produced directly as a copolymer of acrylamide and acrylic acid (Levitt and Pope 2008).

The tendency of PAM to be adsorbed and the retention of PAM and other polymers on reservoir rock surfaces can be due to both mechanical entrapment and chemical adsorption (Hollander, Somasundaran et al. 1981). In some cases mechanical entrapment is a major reason for PAM retention. Many factors are responsible for the adsorption of PAM on rock surfaces such as ionic strength, temperature, polymer molecular weight, surface charge, and the functional group distribution (Kurşun, Ipekoğlu et al. 2000; Samoshina, Diaz et al. 2003). Agnes et al. (Hollander, Somasundaran et al. 1981) studied the adsorption of PAM on sodium kaolinite, and for non-ionic PAM, the adsorption on charged surfaces is mainly due to hydrogen bonding between the amide group and charged surface (Atesok, Somasundaran et al. 1988). With the increase in the polymer concentration, adsorption increases initially and at high concentrations a plateau is observed (Page, Lecourtier et al. 1993). The pH does not affect the adsorption density of non-ionic PAM and the temperature strongly affects the adsorption isotherm of PAM in an inverse relationship. PAM is uncharged initially but at high temperature hydrolysis forms some charges on PAM and decreases the hydrogen bonding, which helps in reducing adsorption. This causes an increase in electrostatic repulsion and a decrease in adsorption (Hollander, Somasundaran et al. 1981). Adsorption of PAM on sandstone rocks increases in the presence of calcium (Lee, Lecourtier et al.),and the presence of a non-ionic surfactant increases the adsorption of non-ionic polymer on silica (Samoshina, Diaz et al. 2003).

2.2.2 Partially Hydrolyzed Polyacrylamide

Commercially available water soluble PAM used for cEOR is a copolymer of acrylamide (AM) and acrylic acid or its salts and is known as HPAM. HPAM, the structure of which is shown in Figure 2-2, is the most widely used polymer for cEOR applications (Niu, Ouyang et al. ; Sabhapondit, Borthakur et al. 2003; Zhang, Zhou et al. 2008; Seright, Fan et al. 2011; Xu, Xu et al. 2012; Wakasiki, Liu et al. 2014) and a number of publications has reported its evaluation under different conditions (Szabo 1979; Shupe 1981; Dupuis, Lewandowski et al. 1994; Bradna, Quadrat et al. 1995; Broseta, Medjahed et al. 1995; Sukpisan, Kanatharana et al. 1998; Peng and Wu 1999; Ghannam and Esmail 2002; Hou, Liu et al. 2005; Gong, Xu et al. 2008; Rashidi, Blokhus et al. 2010; Samanta, Bera et al. 2010). In the following sections, the thermal stability, rheology and adsorption of HPAM on rock surface will be discussed.

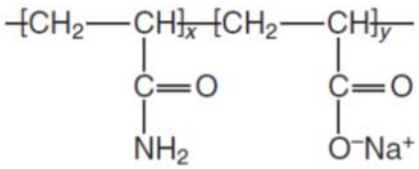

Figure 2-2: Structure of HPAM (Nasr-El-Din, Hawkins et al. 1991)

2.2.2.1 Thermal Stability of HPAM

The percentage of acrylate groups in HPAM is referred to asthe degree of hydrolysis (DOH).The negative charge induced by hydrolysis increases the polymer viscosity due to increased repulsion between the HPAM chains. However, a higher degree of hydrolysis is not always advantageous in all cases, as precipitation can occur in the presence of

divalent cations. Zaitoun et al. (Zaitoun and Potie)reported 33% as a critical degree of hydrolysis for precipitation in the presence of divalent cations at 80^{o}C. Even if there is no precipitation, strong interactions of cations with the carboxylate group can lead to a reduction in the viscosity of HPAM (Wu, Wang et al. ; Zaitoun and Potie ; Ryles 1988; Sabhapondit, Borthakur et al. 2003; Lu, Feng et al. 2010). However, when the amount of divalent cations is negligible (< 200 ppm), the solution viscosity retention is very high (Ryles 1988).

The rate of hydrolysis strongly depends on temperature and pH (Lu, Feng et al. 2010). Ryles (Ryles 1988) found that that the rate of hydrolysis is rapid at 90°C, moderate at 70°C, and negligible at 50°C. While about 90% DOH is reached within few days of aging at 100^{o}C (Audibert and Argillier 1995), at 83 ^{o}C about 70% DOH is reached within 100 days at neutral pH (Levitt, Dufour et al.). Moradi et al.(Moradi-Araghi, Cleveland et al. 1987) also concluded that in the presence of divalent cations the maximum temperature limit is 75^{o}C. All of the above mentioned studies were conducted in the presence of divalent cations, and the use of HPAM was recommended up to 100^{o}C when the concentration of divalent cations is less than 200 ppm (Levitt and Pope 2008). Subsequently it was found that in the absence of divalent cations, HPAM maintained half of the original viscosity at 100^{o}C for 8 years and at 120^{o}C for 2 years (Seright, Campbell et al. 2010). Hydrolysis rate is low at neutral pH and increases in acidic or basic pH regions (Levitt, Pope et al. 2011)**.**Therefore, if reservoir brine has divalent cations (>200 ppm) application of HPAM should be restricted to 70^{o}C. However, if reservoir brine contains less than 200 ppm divalent cations HPAM is safe to use up to 100^{o}C.

2.2.2.2 Rheology of HPAM

Normally HPAM exhibits Newtonian behavior at low shear rates and non-Newtonian behavior at high shear rates. Non-Newtonian behavior includes both shear thinning and shear thickening regions (Nasr-El-Din, Hawkins et al. 1991; Ghannam and Esmail 1998; Lewandowska 2007).The shear-thickening behavior is normally observed after a critical shear rate. The value of the critical shear mainly depends on the degree of hydrolysis, molecular weight, polymer concentration, and temperature (Hu, Wang et al. 1995; Lewandowska 2007). Salts significantly reduce the viscosity of HPAM aqueous solutions due to the charge shielding effect (Martin, Hatch et al. 1983; Sukpisan, Kanatharana et al. 1998), but still it is better than non-ionic PAM (Sabhapondit, Borthakur et al. 2003). PAM chain is very flexible and extremely sensitive to shear degradation (Shah 1977).The incorporation of the acrylate group makes the chain rigid due to charge repulsion (Flew and Sellin 1993). Thus, HPAM is less sensitive to shear degradation than PAM, and high molecular weight HPAM is more sensitive to shear degradation when compared to low molecular weight HPAM (Martin 1986). High shear rates may be encountered during pumping and near the well bore area. High molecular weight of HPAM also makes it less suitable for oil reservoirs with low permeability (Zhong, Luo et al. 2009). It was found that the viscosity of some high molecular weight polymers was low when compared to the viscosity of low molecular weight polymers after shearing (Zaitoun, Makakou et al. 2012). Only few studies have been conducted on the effect of pressure on HPAM viscosity. The intrinsic viscosity and the radius of gyration of HPAM are independent of pressure(Cook, King Jr et al. 1992). Temperature has an adverse effect on the viscosity of HPAM and thermo-thinning behavior has been reported for HPAM (Ghannam and

Esmail 1998). Three types of HPAM-surfactant interactions, depending upon the nature of the surfactant and polymer, can be observed (Methemitis, Morcellet et al. 1986). Firstly, the attractive forces between the surfactant and the polymer may be higher compared to mutual interaction of the surfactant molecules (cationic surfactant-HPAM). Secondly, polymer molecules may associate with micelles formed by the surfactant (non-ionic surfactant-HPAM). In this case, attractive forces between the surfactant and the polymer are weaker when compared to the forces between the surfactant molecules. Thirdly, surfactant-polymer binding does not occur if there is strong repulsive forces between the surfactant and HPAM (anionic surfactant-HPAM) (Methemitis, Morcellet et al. 1986). Non-ionic surfactants do not have an effect on the rheological properties of HPAM, while the addition of anionic surfactants slightly reduces the viscosity of HPAM (Nasr-El-Din, Hawkins et al. 1991; Xin, Xu et al. 2008). Alkaline conditions can affect HPAM both physically and chemically. The viscosity of HPAM is reduced by charge shielding and enhanced by hydrolysis (Nasr-El-Din, Hawkins et al. 1991). The net effect of alkaline conditions depends on the extent of charge shielding and hydrolysis. Recently, nano particles were used to enhance the stability and viscosity of HPAM aqueous solutions (Silva, Oliveira et al. 2013). In general, rheological behavior of HPAM depends mainly on reservoir temperature, salts present in reservoir brine, shear experienced during injection, molecular weight and interactions with surfactant in case of surfactant-polymer flooding.

2.2.2.3 Adsorption of HPAM

Typically the surface charge on sandstone is negative while it is positive on carbonate. Higher DOH decreases the adsorption in sandstone reservoirs due to the large number of

COO^- groups in HPAM. Adsorption of HPAM is very high in carbonate reservoirs when compared to sandstone reservoirs. Unlike non-ionic PAM, electrostatic attraction between the reservoir rock surface and the charged polymer plays a major role in the adsorption of the polymer (Atesok, Somasundaran et al. 1988). Therefore, the strong interaction between Ca^{2+} and COO^- groups results in high adsorption of HPAM in carbonate reservoirs. Salinity also has an adverse effect on adsorption of HPAM in sandstone reservoirs. High salt concentration introduces cations that promote interaction between the sandstone rock surface and the polymer by reducing the size of HPAM flexible chain, which leads to high adsorption (Lee, Lecourtier et al. ; Lecourtier, Lee et al. 1990; Cook, King Jr et al. 1992). High temperature causes an increase in the negative charges on the rock surfaces (Sheng 2010), which increases the electrostatic repulsion and decreases adsorption. Permeability is another important factor that influences the retention of polymers in the reservoir rock (Sheng 2010). Mechanical entrapment is higher in low permeability rock when compared to high permeability rock.

Unlike non-ionic PAM, the isoelectric point of mineral surfaces and pH are important factors in deciding the adsorption isotherm. Isoelectric point is defined as the pH at which a particular surface or molecules carries no net electrical charge. Isoelectric point of kaolinite is 4.7 and if the pH is greater than 4.7, adsorption of HPAM will be low and decreases further with increasing pH. A pH greater than 4.7 will induce negative charges on the mineral surface and adsorption will decrease due to electrostatic repulsion. Similar results for HPAM adsorption have been obtained for silicon carbide (Lecourtier, Lee et al. 1990) and iron oxide (McGuire, Addai-Mensah et al. 2006). HPAM adsorption and retention has been shown to be concentration independent in dilute and concentrated

region (Seright and Zhang), while it is concentration dependent in the semi dilute region. Also, it was proposed that polymer retention can be decreased by first injecting a solution with a low-polymer concentration. In the dilute region, polymer molecules exist as free coil and almost all of the molecules are in contact with the rock surface. In the concentrated region all the sites of the rock are covered by the polymer molecules. Therefore, concentration has no effect in these two regions. In the semi dilute region there is mixed adsorption, where full segments of some of the molecules are adsorbed while others are only partially adsorbed.

In summary, application of HPAM is limited to 75^{o}C in the presence of divalent cations. However, in the presence of negligible amounts of divalent cations (<200 ppm), application of HPAM can be extended to 100^{o}C. Most of the reservoirs with residual oil have more hostile conditions of temperature and salinity (Chen, Song et al. 1998; Han, AlSofi et al. 2013). From the above discussion it is clear that both PAM and HPAM have deficiencies and need some modification or replacement for cEOR in reservoirs having high salinity and high temperature. Many attempts have been made to improve the performance of EOR polymers for high-salinity and high-temperature reservoirs by modifying the structure of PAM and HPAM. Many approaches are used for the modification of PAM. The most common method to extend the application of acrylamide (AM) based polymers is copolymerization of AM with suitable monomers that can increase the stiffness and rigidity of the polymer chain (Khune, Donaruma et al. 1985; Sabhapondit, Borthakur et al. 2003). Modified PAM can be divided into three categories. The first category consists of those copolymers or terpolymers synthesized by incorporating rigid or stiff monomers. These monomers are more resistant to chemical

degradation, more resistant to cation shielding, and can sterically hinder the polymer chain to keep the hydrodynamic radius at a reasonable value at high salinity. A list of some monomers is provided in Table 2-1. The second category includes those polymers synthesized by incorporating a hydrophobic monomer so that intermolecular association can enhance the viscosity. The third category consists of PAM based thermo-viscosifying polymers having a thermosensitive monomer on the main hydrophilic chain. Subsequent sections will highlight selected polymer systems that are synthesized by modifying PAM or other classes of polymers.

2.2.3 Modified polymers

2.2.3.1 Copolymer of Acryl amide and 2-Acrylamido-2-Methylpropane Sulfuric Acid

The thermally stable 2-acrylamido-2-methylpropane sulfuric acid (AMPS) monomer can be copolymerized with AM to obtain a water soluble anionic polymer with improved thermal stability. The structure of AM-AMPS copolymer is shown in Figure 2-3.Several investigations of laboratory evaluation of AM-AMPS copolymer for EOR applications(Han, Zhou et al. ; McCormick and Chen 1982) have been reported. Incorporation of the AMPS monomer in AM also improves the solubility of the polymer in the presence of divalent cations(Rashidi, Blokhus et al. 2010).

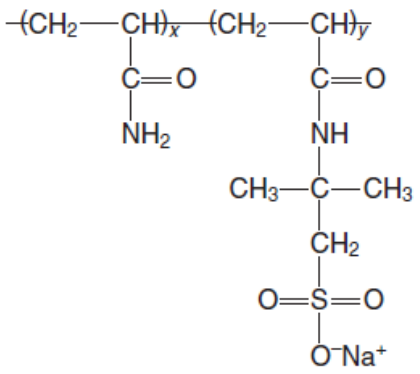

Figure 2-3: Structure of the AM-AMPS copolymer

Table 2-1: Some monomers reported in the literature to enhance PAM performance

Monomer	Reference
Sodium vinyl sulfonate	(Xu, Gao et al. 2011)
Sodium 3-methacrylamido-3-methylbutan-oate	(Xu, Gao et al. 2011)
N-vinyl-2-pyrrolidinone	(Xu, Gao et al. 2011)
Diacetone acrylamide (DAAM)	(Levitt and Pope 2008)
2-acrylamido-2-methylpropane sulfonic acid	(Moradi-Araghi, Cleveland et al. 1987)
N-methyl, N-isopropyl, N-n-butyl, and N-t-butyl acrylamide	(Khune, Donaruma et al. 1985)
2-acrylamido-2-methylpropanedimethylammonium chloride	(McCormick and Blackmon 1986)
N-vinyl-2-pyrrolidone	(Doe, Moradi-Araghi et al. 1987; Kiatkamjornwong and Suwanmala 1998)
[2-(acrylamido)-2-methylpropyl] trimethylammonium chloride.	(McCormick and Salazar 1992)
3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1 propanesulphonate	(McCormick and Salazar 1992)
Sodium 3-acrylamido-3-methylbutanoate	(McCormick, Middleton et al. 1992)
4-(2 -acrylamido-2-methylpropanedimethylammonio) butanoate	(Kathmann and McCormick 1997)
1,3-oxazolic	(Vega, Sánchez et al. 2008)
Carboxymethylcellulose	(Yang, Li et al. 2009)
Mono-2-O-(allyl oxygen radicals-2-hydroxyl propyl)- β -cyclodextrin (O- β -CD)	(Liu, Jiang et al. 2013)
Mono-6-(allyl amino)-β-cyclodextrin (A- β-CD)	(Liu, Jiang et al. 2013)
N,N-didecyl-N-methyl-N-(4-vinylbenzyl)ammonium chloride	(Kuang and Xia 2014)
Allyl polyoxyethylene-12 ether with butyl-end group (AE12B)	(Zhou, Yang et al. 2011)
Ether carboxylate	(Bai, Za et al. 2012)
N-phenylmaleimide	(Liu, Jiang et al. 2012)
p-styrenesulfonate	(Ye, Gou et al. 2013)
Sodium (acrylamido) methanesulfonate	(Ye, Gou et al. 2013)

2.2.3.1.1 Thermal Stability of Am-Amps Copolymer

Moradi et al.(Moradi-Araghi, Cleveland et al. 1987) evaluated the AM-AMPS copolymer with a low AMPS content at 120^{o}C. Although precipitation was observed at this temperature in seawater of 33,560 ppm, increasing AMPS content to 91% showed negligible precipitation. Using a high AMPS percentage has a couple of disadvantages; namely, AMPS is a more expensive monomer compared to AM and the homo polymer of AMPS is not a good viscosifier. They reported the optimum conditions for application of the polymer as a 40% AM content and a maximum of 93^{o}C at a maximum salinity level of 33,560 ppm. Ryles (Dexter and Ryles 1989)observed that the rate of hydrolysis decreased with increasing AMPS concentration. Parker (Parker and Lezzi 1993) discovered that AMPS itself hydrolyzes at temperatures higher than 120^{o}C with AMPS hydrolyzing after 55 days, while at 150^{o}C the same degree of hydrolysis was reached within only 4 days. Both internal and external hydrolysis is supposed to be involved. External and internal hydrolysis take place through the direct attack of OH^- ions on AMPS and intermolecular catalysis, respectively (Parker and Lezzi 1993). At temperatures less than 90 ^{o}C hydrolysis of AMPS was not observed even at alkaline pH. The rate of hydrolysis is also strongly dependent on pH. In acidic pH the rate of hydrolysis was very high compared to the rate in the basic pH range. The rate of hydrolysis of AMPS increased five-folds when the pH was decreased from 8 to 6.In the basic pH region, strong repulsion between OH^- and the polymer chain lowers the rate of hydrolysis. Audibertet al.(Audibert and Argillier 1995)evaluated the copolymer with 13% AMPS content. They observed that aging of the polymer solution in 30g/L KCl at 90^{o}C for 20 days had no effect on the intrinsic viscosity. The same solution lost one third of its

viscosity within 10 days when aged at 130^{o}C. Residual impurities of the polymerization process also cause thermal instability(Noik, Audibert et al. 1994),with a highly purified solution showing better thermal stability.

2.2.3.1.2 Rheology of Am-Amps Copolymer

Salinity has a strong effect on the rheology of the AM-AMPS copolymer. Storage and loss moduli decrease due to the addition of salt(Kamal, Hussien et al. ; Kim, Lee et al.). Modulus crossover point of the copolymer did not significantly change with temperature. Rashidi et al. (Rashidi, Blokhus et al. 2010) evaluated the effect of the degree of sulfonation on shear stability and found that the increase in the degree of sulfonation has increased the shear stability due to increased rigidity. The higher rigidity of AM-AMPS copolymer is due to the large hydrodynamic radius of AMPS compared to AM. A similar observation was reported by other researchers(Zaitoun, Makakou et al. 2012).

2.2.3.1.3 Adsorption of Am-Amps Copolymer

At constant salt concentration, the adsorption of AM-AMPS copolymer on kaolinite decreased as the pH is increased(Hollander, Somasundaran et al. 1981). Kaolinite is negatively charged and the AMPS solution contains negative charges. With the increase in pH from 2 to 9 the surface charges on kaolinite will increase. This increase leads to more electrostatic repulsion which will eventually decrease the equilibrium adsorption. Ionic strength was found to be another important factor in the adsorption of AM-AMPS copolymer on kaolinite. As the ionic strength approaches zero, adsorption on kaolinite reaches a minimum. But the increase of the ionic strength increases the adsorption of AM-AMPS copolymer due to the decrease in electrostatic repulsion between kaolinite

and the copolymer caused by charge shielding in the presence of salts (Hollander, Somasundaran et al. 1981).

Adsorption of the sulfonated polymer on limestone,(is electric point of this polymer is at a pH of 8.2), has been studied by Celik et al.(Celik, Ahmad et al. 1991) at a pH of 8. Below the isoelectric point, the surface charge on limestone is positive while above it the surface charge is negative. Without any added salt, adsorption is high due to electrostatic forces induced between the rock surface and the negative charge of the sulfonate group. Adding salt decreases the electrostatic attraction and reduces the polymer adsorption on calcite. Adsorption behavior of the sulfonated polymer is different between sandstone and carbonate reservoirs. Addition of salts has a different impact on the adsorption on carbonate and sandstone reservoirs. Adsorption as a function of the temperature was studied by Agnes et al. (Hollander, Somasundaran et al. 1981) in the range of 30^{o}C to 60^{o}C and found that the temperature in this range has no effect on adsorption both at low and high ionic strength. The copolymer is not sensitive to temperature in this range and very low temperature hydrolysis is expected. Similar adsorption value was observed at 30^{o}C and 60^{o}C due to no net change in the charge on the polymer and rock surfaces (Hollander, Somasundaran et al. 1981).

2.2.3.2 Copolymer of Acryl amide and Vinylpyrrolidone

Vinylpyrrolidone (VP) is another important monomer used to copolymerize with AM for EOR applications. Homo polymer of VP (PVP) has very good thermal stability in aqueous and salt solutions(Bock, Pace et al. 1987). However, PVP is not a good viscosifier and to achieve the equivalent viscosity of HPAM a 10-fold higher

concentration is almost required. The cost of this polymer is 3 times higher than that of PAM(Doe, Moradi-Araghi et al. 1987)and the adsorption of PVP is very high on rock surfaces(Bock, Pace et al. 1987).These two factors make PVP unsuitable for EOR applications due to economic reasons. However, the copolymer of AM and VP has the desirable properties. Moradi et al. (Doe, Moradi-Araghi et al. 1987)found that the addition of VP to AM can decrease the thermal hydrolysis of AM in the presence of divalent cations. The decrease in the hydrolysis is directly proportional to the VP content in the final copolymer. Copolymer of VP and AM is stable at 120^{o}C in the presence of seawater for many months.

The proposed mechanism involves steric hindrance and/or hydrogen bonding between VP and AM; a similar observation was also reported by Kulawardana (Kulawardana, Koh et al. 2012). Adsorption of the copolymer in the sandstone core was low compared to HPAM. Poly (1-vinyl-2-pyrrolidone-*co*-partially hydrolyzed acrylamide) was synthesized by Kiatkamjornwong (Kiatkamjornwong and Suwanmala 1998)and the resulting copolymer has a higher decomposition temperature by about 23^{o}C than the homo polymer of AM. Inclusion of VP on the AM chain increases the shear stability in comparison with the homo polymer of AM due to the large size of the VP group(Zaitoun, Makakou et al. 2012).In summary, VP can better protect AM, but due to the low polymerization activity it is difficult to achieve a high molecular weight polymer (Gaillard, Sanders et al.).

2.2.3.3 Other Acryl amide Based Copolymers

Another approach to improve the viscosity retention of PAM was proposed by Shepitka et al. (Shepitka, Case et al. 1983).They found that the addition of intra molecular imide rings can increase the chain stiffening and the viscosity retention. Khune et al.(Khune, Donaruma et al. 1985) synthesized a copolymer of sodium acrylate and N-alkyl acrylamide and found that N-Methyl substitution into the polymer backbone decreases the polymer retention in sandstone reservoirs. The salt tolerance is slightly increased by replacing the hydrogen of the amide group with a methyl group. Disadvantage of introducing the methyl substitution is that it makes the polymer more shears sensitive. However, better viscosity retention compared to analogous HPAM was observed. Sabhapondit synthesized *N*,*N*-dimethyl acrylamide (NNDAM)-sodium AMPS (NaAMPS) copolymer with 41% AMPS content and stability at 120^{o}C was reported and the viscosity retention was about 66% after a month of aging. Due to the absence of free (-$CONH_2$) group, thermal hydrolysis does not take place. For the NNDAM-Acrylic acid (AA) copolymer, a total viscosity loss was detected after few days at 120^{o}C.

In another modification proposed by Uhl et al. (Uhl, Ching et al. 1995), a terpolymer was synthesized which contains ionic surfactant molecules as side chains of the acrylamide-sodium acrylate copolymer. Salt tolerance was increased compared to conventional HPAM by salt induced surfactant chain aggregation, which occurs only at higher concentrations. Although a higher viscosity was reported compared to HPAM, the thermal stability of these polymers was not better than HPAM; and therefore, they are not

good candidates for high temperature reservoirs. Due to strong shear thinning properties, injectivity is better compared to HPAM.

Another class of AM modified polymer is the comb type polymer, which consists of both hydrophilic and lipophilic groups on the same chain segments. Due to the mutual repulsion, the polymer forms a comb shape and the chain becomes rigid due to the increased hydrodynamic radius. Atypical structure of the comb type polymer is shown in Figure 2-4 (R1, R_2, and R_3 maybe either H or an alkyl chain (C_1-C_{12}) and A is a Ca^{2+}or Mg^{2+} tolerant ionic functional group). The groups R_1, R_2, and R_3 are mainly related to the elasticity of the polymer (Sheng 2010). The higher the carbon number in $R_4$the higher the elasticity and $R_4$is related to the salinity tolerance of the polymer. Xu et al. (Xu, Gao et al. 2011) synthesized a comb polymer of acrylamide and non-ionic amphiphilic macromer (OPAE),which was synthesized using AA and t-octylphenoxypolyoxyehylene (OP) by an esterification reaction. The intrinsic viscosity was observed to be better for the macromere in salt solution compared to HPAM. Several investigations discuss the application of comb shaped polymers in EOR(Zhao, Zhou et al. 2009; Wu, Long et al. 2013). Other amphiphilic monomers reported in the literature are: allyl polyoxyethylene-12 ether with butyl-end group (Zhou, Yang et al. 2011) and carboxylate ether (CE)(Bai, Za et al. 2012).

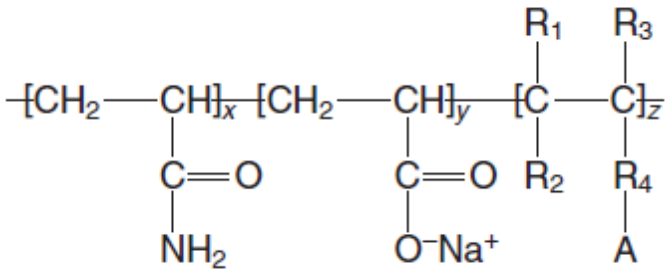

Figure 2-4: Structure of a comb type polymer (Sheng 2010)

Liu et al. (Liu, Jiang et al. 2012) synthesized a sulfonated copolymer of acrylamide (AM) and N-phenylmaleimide (N-PMI)and reported a 60 % viscosity retention at 85^{o}C and a 9.5 % additional oil recovery for the sulfonated copolymer. Ye et al. synthesized AM-*N*-allylbenzamide (NABI)copolymer of AM-NABI and AM-NABI-sodium (acrylamido) methane sulfonate (SAM) terpolymer, for which salt and temperature tolerance were better than HPAM but viscosity retention was only 25% at 120^{o}C.Poly (acrylic acid-*st*-1-vinyl-2-pyrrolidone) was synthesized using acrylic acid andN-vinyl-2-pyrrolidinone monomers instead of AM (Kotsuchibashi, Doda et al.),which showed a strong resistance to alkali and a better oil recovery compared to HPAM. Under similar conditions 47% recovery was reported compared to 41% recovery with HPAM. However, the molecular weight of the copolymer is almost half of the molecular weight of HPAM. The copolymer has a higher injectivity and a lower retention compared to HPAM.

In summary, several attempts have been made to improve performance of polyacrylamide by using more salt tolerant and temperature tolerant monomers. Copolymers synthesized

using these monomers has increased the temperature and salinity limits of acrylamide based water soluble polymers in cEOR.

2.2.4 Hydrophobically Modified Associating Polymers

Hydrophobically modified associating (HMA) polymers consist of a water soluble backbone modified with a small fraction of a hydrophobic monomer, and in aqueous solutions the hydrophobic groups associate and make hydrophobic micro-domains(Berret, Calvet et al. 2003). HMA polymers can be synthesized by grafting hydrophobic moieties on a water soluble chain or copolymerizing a hydrophobic monomer with a water soluble monomer (Argillier, Audibert et al. 1996). Hydrophobes can be incorporated into water soluble chains in several ways depending on the method of synthesis. Based on the distribution of hydrophobic moieties, HMA polymers can be classified into 4 different categories. These include: associative polymers containing only one associating block, telechelic, multisticker and combined HMA polymers (Volpert, Selb et al. 1998; Chassenieux, Nicolai et al. 2011; Perttamo 2013). From the description, the first class consists of those HMA polymers in which hydrophobes are present on only one end of hydrophilic chain. Telechelic HMA polymers contain hydrophobic groups on both ends. Multisticker HMA polymers have several hydrophobic groups along the chain(Perttamo 2013). To ensure water solubility, hydrophobic monomer concentration is normally kept at less than 5% (Argillier, Audibert et al. 1996),and in a dilute solution regime, intra molecular associations take place leading to coil contraction.

However, above a critical association concentration (CAC), intermolecular associations dominate over intra molecular associations resulting in the formation of a network

structure (Lu, Feng et al. 2008). Formation of the network structure can enhance the viscosity of the polymer which can be controlled by many external and internal factors. Some of the first hydrophobically modified associating polymers were synthesized in late 1960s (Dubin and Strauss 1967; Dubin and Strauss 1970) by copolymerizing maleic acid and alkyl vinyl ether. Acrylamide based HMA polymers were synthesized in the 1980s for EOR applications. A large number of publications are available on lab scale evaluation of HMA polymers for cEOR applications(Guo, Liu et al. 2012). A list of hydrophobic monomers is given in the Table 2-2.

Table 2-2: Hydrophobic monomers reported in the literature

Hydrophobic group	**Ref**
2-vinylnaphtahlene	(Zhong, Luo et al. 2009)
Nonyl methacrylate	(Argillier, Audibert et al. 1996)
2-(methacryloyloxyl) ethylhexadecyldimethylammonium Bromide	(Lu, Feng et al. 2008)
N-4-ethylphenyl acrylamide	(Hill, Candau et al. 1993)
Dimethyl dodecyl(2-acry1amidoethyl)ammonium bromide	(Chang and McCormick 1993)
N-dodecyl methacrylamide	(Hashidzume, Yamamoto et al. 1999)
Nonyl methacrylate	(Argillier, Audibert et al. 1996; Starkey, Davis et al. 2000)
n-alkyl(meth)acrylate	(Ma, Huang et al. 2005)
Poly[ethoxy alkyl-(meth)acrylate]	(Ma, Huang et al. 2005)
Vinyl alkylates	(Ma, Huang et al. 2005)
N-arylalkylacrylamide (BAAM)	(Volpert, Selb et al. 1996; Ma, Huang et al. 2005)
Octyl bromide	(Feng, Billon et al. 2002; Feng, Grassl et al. 2002)
N-phenyl acrylamide	(Abu-Sharkh, Yahaya et al. 2003)
Octyl alkyl group	(Feng, Billon et al. 2005)
t-octylacrylamide	(Gouveia, Paillet et al. 2008)
N,N-dihexylacrylamide	(Maia, Borsali et al. 2009)
N,N-dihexylacrylamide	(Maia, Borsali et al. 2009)
Poly(propylene glycol) monomethacrylate,	(Gouveia, Grassl et al. 2009)
5,5,5-triphenyl-1-pentene	(Niu, Ouyang et al. ; Zhang, Wang et al. 2011)
N,N-divinylnonadeca-1,10-dien-2-amine (DNDA)	(Lai, Dong et al. 2012)
N-allyloctadec-9-enamide (NAE)	(Ye, Feng et al. 2013)

2.2.4.1 Rheology of HMA Polymers

The nature and length of the hydrophobic chain influences the association behavior of HMA polymers, and an increase in the hydrophobic chain length increases the viscosity of HMA polymer (Niu, Ouyang et al.).*N*-methyl-*N*-hexylacrylamide has a low viscosity even if high amount (5 %) is used. On the other hand, *N*, *N*-dihexylacrylamide co monomer even at low ratios (1 %) provide strong association and a high viscosity(Volpert, Selb et al. 1998). HMA polymers with blocky microstructure develop strong association and viscosification compared to HMA polymers with random distribution (Tanaka, Williams et al. 1992; Hill, Candau et al. 1993; Volpert, Selb et al. 1998).Double tail hydrophobes are more effective and provide more viscosification compared to single tail hydrophobes (Volpert, Selb et al. 1996). The viscosity is normally directly proportional to the hydrophobic monomer content(Niu, Ouyang et al.). But there is always an optimum concentration of the hydrophobic monomer and further increase reduces the viscosity(Zhong, Luo et al. 2009). In HMA terpolymer containing AM, AMPS, and 2-vinylnephthalene (VN), the solution viscosity increased when the hydrophobic monomer VN content was increased up to 0.75%. However, at a 1 % hydrophobic content the viscosity reached a minimum. At low monomer concentration, hydrophobic association results an increase in the viscosity enhancement. However, at higher hydrophobic monomer concentration phase separation decreases the viscosity.

For HMA polymers the addition of salts, results in a change of the rheological properties. Depending on the concentration of the polymer, the viscosity of HMA polymers may increase or decrease by changing the salinity. In the dilute region, the presence of salts

increases the intramolecular interactions which may decrease the viscosity of HMA polymers. In the semi-dilute region, the presence of salts increases the intermolecular associations and the viscosity will increase. This type of behavior was also observed for HMA polymer–surfactant systems(Gouveia, Paillet et al. 2008). At a fixed polymer concentration, an optimum salinity was obtained for most HMA polymers. The viscosity of the HMA polymers increases with salt concentration up to a critical salt concentration and a further increase in the salt concentration reduces the viscosity. The initial increase in the viscosity is normally due to increased polarity by electrolyte addition, which enhances the intermolecular association. But above the critical concentration, intra molecular association increases and the hydrophobic structure becomes more compact. The enhanced intra molecular association can result in phase separation and viscosity reduction(Zhong, Luo et al. 2009).

In general, the viscosity of HMA increases gradually with the increase in polymer concentration. However, for HMA polymers the viscosity change with the change in polymer concentration is abrupt (Niu, Ouyang et al.). This is due to the aggregation of the hydrophobic groups and physical cross linking. For most HMA polymers, the viscosity versus temperature has a maximum at a specific temperature. The initial increase in the viscosity with temperature is due to the increase in association as it is an entropy-driven endothermic process. But after a specific temperature, the viscosity decreases due to the reduction in the association (Niu, Ouyang et al. ; Lai, Dong et al. 2012). A similar observation was made for HMA polymers containing 2-vinylnephthalenehydrophobic monomers.

Shear resistance of HMA polymers is also improved when compared to un-modified counterparts(Lijian and Biao). Zhou et al. (Zhou, Dong et al.) found that in the semi-dilute region and in the presence of sodium dodecyl benzene sulphonate, HMA polymer showed a shear-thickening behavior. Shear- thickening behavior at low shear rate is due to the transformation from intra molecular association to intermolecular association(Zhong, Luo et al. 2009).

Presence of surfactants may enhance or reduce the viscosity of the HMA polymers depending on the concentration of the added surfactant and the competition between intermolecular and intra molecular association. Sodium dodecyl benzene sulphonate enhances the viscosity of HMA polymers at low concentration due to formation of network structure. But at high concentration the viscosity decreases due to disruption of associated structures(Zhou, Dong et al.). Similar behavior was observed with sodium dodecyl sulfate (Gouveia, Paillet et al. 2008).Critical association concentration shifts at lower polymer concentration by increasing the polymer molecular weight. In summary, rheological properties of HMA polymers are different compared to the un-modified polymers and depend mainly on: hydrophobe type and chain length, hydrophobe distribution, concentration of hydrophobic group, temperature, polymer concentration and salt concentration. Due to the favorable rheological properties, different research groups around the world are trying to extend applications of HMA polymers to high-temperature high-salinity (HTHS) reservoirs.

2.2.4.2 Adsorption of HMA Polymers

The adsorption behavior of HMA polymers is different when compared to the un-modified counterpart, with the hydrophobic moieties playing an important role in the adsorption of HMA polymers. Unlike the un-modified polymers, adsorption isotherms of HMA polymers show an unusual shape characterized by a continuous increase in the adsorption with the polymer concentration without a plateau region(Volpert, Selb et al. 1998; Nilsson and Bergenståhl 2007). This unusual shape is due to the multilayer adsorption of HMA polymers on mineral surfaces as proposed by Page et al. (Page, Lecourtier et al. 1993). Inner layer is linked to the mineral surfaces by hydrogen bonding and the loosely bound outer layer is attached to the inner layer through hydrophobic interactions. Hydrophobic moieties can also interact directly with the mineral surfaces(Volpert, Selb et al. 1998).The adsorption of HMA polymers is high compared to unmodified counterparts(Zhang, Wang et al. 2013).

Adsorption is usually low for HMA polymers with random monomer distribution when compared to HMA polymers with blocky microstructure due to hydrophobic association(Tanaka, Williams et al. 1992; Ren, Li et al. 2008). Blocky distribution of monomer helps in developing strong hydrophobic interactions which lead to high adsorption. Adsorption of HMA polymers decreases with an increase in the solid/liquid ratio, which is due to the reduction of the surface that is accessible to polymer due to aggregation (Page, Lecourtier et al. 1993). For the un-modified polymer, a classical adsorption isotherm is normally observed, i.e., adsorption increases with polymer concentration initially then a plateau is reached. HMA Polyacrylamide adsorption

continuously increases with increasing polymer concentration due to multi-layer adsorption(Starkey, Davis et al. 2000). Adsorbed layer directly in contact with the mineral surface has some segments in contact with the rock surface, while the remaining segments associate with other chains due to hydrophobic interactions (Page, Lecourtier et al. 1993; Huang and Santore 2002). Due to these hydrophobic interactions, adsorption continuously increases with increasing polymer concentration. The adsorption of HMA PAM is high when compared to PAM and this difference is attributed to the additional adsorption caused by hydrophobic interactions(Lu, Feng et al. 2008). Schematic representation of adsorption is shown in Figure 2-5.

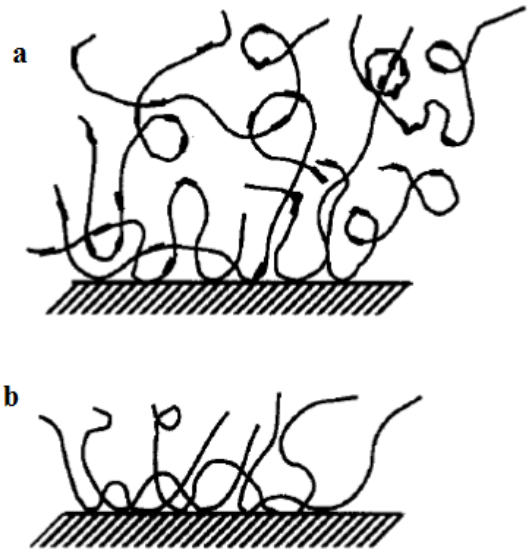

Figure 2-5: Schematic representation of the adsorption of (a) HMA PAM and (b) PAM (Argillier, Audibert et al. 1996)

For HMA polymers, adsorption initially decreases with increasing salt concentration, but above a certain concentration the adsorption increases with increasing salinity. Increase

in the adsorption is due to the enhancement in the hydrophobic interactions that can contribute to multilayer adsorption(Argillier, Audibert et al. 1996). Adsorption of the HMA polymers decreases with the addition of surfactants, which is due to either preferential adsorption of the surfactant or the reduced hydrophobic interactions owing to the presence of the surfactant(Argillier, Audibert et al. 1996). For HMA polymers, molecular weight is directly related to the adsorbed amount (Volpert, Selb et al. 1998). In summary, adsorption density of HMA polymers is usually high compared to un-modified polymers due to multi-layer adsorption.

2.2.4.3 Some Selected HMA Polymers

Feng et al.(Feng, Billon et al. 2002; Feng, Grassl et al. 2002) prepared HMA-HPAM and HMA-PAM using octyl bromide as a hydrophobic group and the effect of salinity on rheological properties of the associated polymer was reported. In the dilute solution regime, an increase in the salinity caused a decrease in the viscosity of both HMA-HPAM and HMA-PAM. However, in the semi-dilute solution regime the salt enhances the viscosity of HMA-PAM due to intermolecular association. Similar behavior was reported for HMA-PAM containing nonyl methacrylate as the hydrophobic group(Argillier, Audibert et al. 1996).Viscosity of HMA-HPAM initially decreased and then increased due to the competing effects of electrostatic and hydrophobic association.

Adsorption of HMA-PAM increased with increasing KCl concentration due to increased hydrophobic interactions (Argillier, Audibert et al. 1996). Maet al. (Ma, Cui et al. 2002) synthesized copolymers of AM and N-aryl alkyl acrylamide by micellar copolymerization where the viscosity increased in the presence of salts. Terpolymer of

acrylamide, 2-acrylamide-2-methylpropanesulfate (AMPS), and hydrophobic monomer N-aryl alkyl acrylamide (BAAM) were also synthesized by the same group(Ma, Huang et al. 2005)and the effect of hydrophobic content was studied. It was reported that increasing BAAM concentration significantly increases the intermolecular association and viscosity. But increasing the concentration of BAAM decreases the solubility of the terpolymer, making it completely insoluble when BAAM concentration is greater than 1.2%. The viscosity of polymer solution increased with increasing salt concentration up to 0.2mol/L after which the viscosity decreased. This concentration dependence is related to the competing effects of the increase in intermolecular association and charge shielding. Practically most reservoirs have much higher salinities than this and the effects of divalent ions and temperature were also not reported in this study.

Feng et al. (Feng, Billon et al. 2005) synthesized HMA polymers containing octyl alkyl as a hydrophobic group. In dilute region, although the viscosity decreased with increasing salinity but the viscosity of the hydrophobic polymer was higher compared to that of PAM. In the semi-dilute region, the viscosity of AMA HPAM increased with increasing salinity due to inter chain association. Moreover, shear thickening behavior was reported in the semi-dilute region. A terpolymer in which the AM hydrophilic backbone was modified with AMPS and hydrophobic monomer 2-vinylnaphtahlene was synthesized by Zhong et al. (Zhong, Luo et al. 2009). It was synthesized to be used in medium and low permeability oil reservoirs with high-salinity and high-temperature. In comparison with PAM, this terpolymer showed improved rigidity and increase in the viscosity with salts and temperature in laboratory testing. The polymer also showed thixotropic behavior and field or pilot plant data were not reported for this polymer.

Feng et al. (Feng, Guo et al. 2013) synthesized hydrophobic PAM containing 0.5% hydrophobic monomer cetyl dimethylallyl ammonium chloride. Thermal stability was measured for 120 days and the polymer was found to be stable, but the investigation was conducted at a temperature of 45^{o}C. High temperature data are not available and it is expected that the polymer is not stable at higher temperatures due to the absence of any other monomer which can protect AM. It is reported that polymer usage was reduced to 40% due to high viscosity retention and a 25% additional oil recovery was reported. A terpolymer of AM, 2-trimethylammonium ethyl methacrylate chloride (TMAEMC) and 5,5,5-triphenyl-1-pentene (hydrophobe) was also synthesized by Zhang et al [147]. Resulting polymer showed better temperature stability up to 50^{o}C.More recently, a terpolymer based on acrylamide, sodium vinyl sulphonate and N, N-didecyl-N-methyl-N-(4-vinylbenzyl) ammonium chloride was synthesized. The apparent viscosity was much higher compared to HPAM (Kuang and Xia 2014).

2.2.4.4 Field Application and Challenges of HMA Polymers

To the best of our knowledge and based on the available literature, the reported applications of HMA polymers in the field are limited. However, extensive lab scale investigations are underway to extend the findings to field applications. One pilot scale test was conducted in Bohai Bay oil field in China using an HMA polymer, where 25000m^3 of incremental oil was recovered and the water cut decreased from 95 to 54% (Zhou, Zhang et al.).

Viscosity of HMA polymers can change abruptly by slightly changing the concentration of the polymer. If the concentration is slightly higher than the optimal value a large

increase in the viscosity may cause infectivity and operational problems. Similarly, a small decrease in the concentration due to polymer retention on rock surface will lead to decrease in the viscosity which will make it insufficient for the desired mobility control (Seright, Fan et al. 2011). Solubility of HMA polymers is also not as good as that of the un-modified counterpart (Langlotz, Brodt et al.).

The mechanism of oil recovery and behavior in porous media of HMA polymers is not well understood and needs further investigations. HMA polymers give rise to viscosity enhancement at concentrations higher than the critical aggregation concentration. Therefore, the apparent viscosity of HMA polymers is higher compared to conventional polymers. However, the effective viscosity of HMA polymers is not as good as that of the conventional polymers probably due to adsorption loss(Zhang, Wang et al. 2012). Another major issue that has not been studied well is the retention and adsorption of polymers on mineral surfaces. Available literature suggests high multilayer adsorption of HMA polymers on mineral surfaces when compared to un-modified polymers.

2.2.5 Thermo viscosifying Polymers

Another important development to enhance the performance of water soluble polymers is the use of thermo-thickening, thermo-associative or thermo-viscosifying polymers (TVP). In early 1990's this property was reported for some water soluble polymer systems by Hourdet et al. (Durand, Hervé et al. ; Hourdet, L'Alloret et al. 1994; L'Alloret, Hourdet et al. 1995; Hourdet, L'Alloret et al. 1997). TVP consist of a water soluble hydrophilic backbone with some hydrophobic pendant side chains. These hydrophobic side chains are soluble in water at room temperature but exhibit a lower critical solution temperature

(LCST). On heating to LCST, the polymer chains start self-aggregation into hydrophobic micro domains to minimize their exposure to water(Petit, Karakasyan et al. 2007).Therefore, TVP can provide viscosity enhancement with temperature by making inter-chain association, which can be several orders of magnitude higher than their unmodified counterparts(Hourdet, L'Alloret et al. 1994).A schematic representation of the association mechanism is shown in Figure 2-6.Addition of salts further enhances the interaction by increasing the polarity of the solvent (Ma, Huang et al. 2005)and another advantage of TVP is that the viscosity can be restored after removing shear.

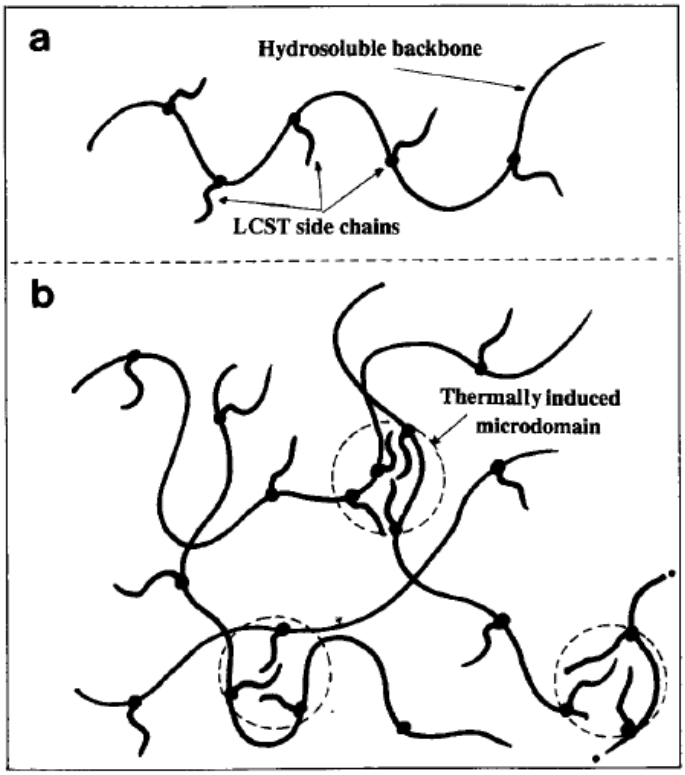

Figure 2-6: Thermo-viscosifying concept in water soluble polymers: (a) copolymer structure; (b) association mechanism (Hourdet, L'Alloret et al. 1994)

Rheology of TVP solutions can be controlled by adjusting external parameters like polymer concentration, salt concentration, temperature, and pH. Degree of grafting, molecular weight, and the chemical nature of the backbone and graft are the most critical internal parameters for thermo-viscosifying behavior(Hourdet, L'Alloret et al. 1997). Strong inter-chain association is possible only above the overlap concentration, C*. Such behavior was initially confirmed with many polymer backbones like, poly (alkaline oxide) semi-dilute solutions of cellulose derivatives, poly (N-substituted acryl amide) derivatives and cellulose ether (Hourdet, L'Alloret et al. 1994; Bromberg 1998).PEO modified polyacrylic acid was among the first generation of this type of thermo-viscosifying polymers(Hourdet, L'Alloret et al. 1994). Lev Bromberg (Bromberg 1998) synthesized another family of TVP where poly(acrylic acid) backbone was modified with plutonic poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO). Synthesis of various types of thermo sensitive polymers was reviewed by Dimitrov et al. (Dimitrov, Trzebicka et al. 2007).The above mentioned polymers have not been reported for EOR applications, but this opens new directions for the synthesis of EOR polymer based on this concept.

Based on the idea proposed by Hourdet, Feng et al.(Wang, Feng et al. 2010; Wang, Lu et al. 2011; Wu, Liu et al. 2012) synthesized a series of TVP for EOR applications. HPAM was modified with various thermo sensitive monomers. It was found that for TVP, the viscosity and storage modulus increase with temperature while for unmodified HPAM viscosity decreases with temperature(Wang, Lu et al. 2011). Under similar conditions, HPAM with high molecular weight (1.2×10^7 g/mol) showed 2.1% oil recovery, while recovery with low molecular weight TVP was more than 13%(Chen, Wang et al. 2013).

A thermo-viscosifying terpolymer, poly (acrylamide-co-2-acrylamido- 2-methylpropane sulfuric acid)-g-poly [acryl amide-co-N-(1,1-dimethyl-3-oxobutyl)acryl amide] (PADAS) was synthesized (Liu, Wang et al. 2012). Terpolymer viscosity was enhanced with increasing salt concentration. Among the investigated cations and anions Na^+ was more effective in enhancing the thermo-viscosifying effect while NO_3^- was the least effective. Under the same conditions AM-AMPS copolymer showed only thermo-thinning behavior while modified terpolymer demonstrated thermo thickening behavior.

In summary, still TVPs have not been applied in reservoirs. The C* value for these polymers is normally high and, as mentioned in the discussion earlier, significant viscosity can only be achieved above C*. TVP seem to be potential candidates for EOR but they are still not available in high enough molecular weight.

2.2.6 Cationic polymers

Only few reports on the use of cationic polymers in cEOR applications are available in the open literature. Most of the reported work has been done in sandstone reservoirs with a negative charge on the matrix rocks. Cationic polymers cannot be used in sandstone reservoirs due to strong interactions between the cationic polymer and the rock particles. Majority of the reservoirs with residual oil are carbonate and these cationic polymers can be an option for carbonate reservoirs.

Fernandez (Fernandez 2005) synthesized a cationic terpolymer of AM-VP and methacrylamide propel trim ethyl ammonium chloride (MP). Increase in the VP content in the terpolymer causes a decrease in the DOH and an increase of the viscosity retention. This behavior was also observed for the copolymers of VP. A copolymer of MP and AM

with 10% MP content achieved 94% DOH after 15 days of aging at 120^{o}C,and further aging at 120^{o}C showed molecular weight degradation. It was also concluded that the size of the AM chain is important for thermal stability, with a polymer having the shortest AM chains showing greater stability due to strong interactions between AM and VP. Another cationic terpolymer of acryl amide, allyl-β-cyclodextrin, and dimethyl diallyl ammonium chloride has been reported(Zou, Zhao et al. 2012). In general, cationic polymers have not been used in cEOR applications and should be considered for lab scale evaluation as they may have less adsorption in carbonate reservoirs.

2.2.7 Biopolymers

The most important polymer in this class is xanthan gum and other polymers of this class include scleroglucan, carboxymethylcellulose, welan gum, and guar gum (Kulawardana, Koh et al. 2012). The term "gum" is usually dedicated to a group of polysaccharides or their derivatives that make a viscous solution at low concentration when dissolved in water (Zohuriaan and Shokrolahi 2004). Gums can be broadly classified as natural gum or modified gum and natural gum can be obtained by the fermentation of microbial organisms (xanthan, welan) or from plant exudates (gum Arabic). Modified gums include starch or cellulose derivatives (Zohuriaan and Shokrolahi 2004).

2.2.7.1 Xanthan Gum

Xanthan gum or simply xanthan is a high molecular bio polysaccharide that is usually produced by the fermentation process of bacterium called Xanthomonas (Cadmus, Jackson et al. 1982; Foss, Stokke et al. 1987; Leela and Sharma 2000; Xu, Xu et al. 2012; Jang, Zhang et al. 2014). The structure of xanthan is shown in Figure 2-7 and the

backbone of xanthan is not much different from cellulose. However, the side chain consists of β-D-manose-1,4-β-D-glucuronic acid-1,2-α-D-manose and the terminal manose is normally a 4,6- linked pyruvic acid ketal (Unsal, Duda et al. 1978; Katzbauer 1998). Xanthan gum proved to be tolerant to divalent cations and can maintain its viscosity under conditions of high salinity (Celik, Ahmad et al. 1991), which is due to the ordering of xanthan molecules at high salinities. In the presence of salts, negatively charged pyruvate molecules wrap around the main chain to make a rigid rod like structure (Dentini, Crescenzi et al. 1984; Celik, Ahmad et al. 1991). Resistance of xanthan to shear and mechanical degradation is much better than polyacrylamide due to the rigidity of the chain (Ash, Clarke-Sturman et al. 1983; Seright, Seheult et al. 2009; Zaitoun, Makakou et al. 2012; Abbas, Donovan et al. 2013). In deionized water, xanthan has a lower viscosity when compared to PAM copolymers at equivalent molecular weight and concentration. However, in saline solutions xanthan has a higher viscosity when compared to PAM copolymers (Sheng 2010).

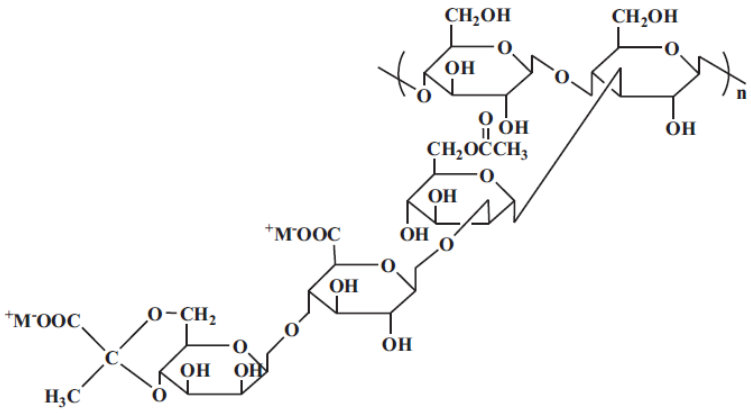

Figure 2-7: Structure of xanthan gum (Bejenariu, Popa et al. 2010)

2.2.7.1.1 Thermal Stability of Xanthan Gum

Xanthan gum molecules consist of a double helix structure at low temperatures, and at high temperatures the double helix structure converts to a disordered coil (Xu, Xu et al. 2012). The temperature limit for xanthan gum was suggested to be <70^{o}C by Ryles et al. (Ryles 1988)and according to Ash et al. [172] xanthan gum was stable at 70^{o}C. However, in another study the polymer was reported as stable at 90^{o}C (Wellington 1983). Milas et al. reported a 50% viscosity retention at 80^{o}C after 6 months, and Seright et al (Seright and Henrici 1990) reported that xanthan retained 50% of the viscosity for at least five years at 75-80^{o}C. Xanthan gum with 60% viscosity retention for 300 days at 80^{o}C and 170,000 ppm salts has also been reported (Han, Yang et al. 1999). At 100^{o}C xanthan is thermally unstable under most of the investigated conditions and the thermal stability depends on the polymer concentration, conformation, and salt content(Lambert and Rinaudo 1985; Kierulf and Sutherland 1988). The variation in the temperature limit reported in the above mentioned studies is probably due to the difference in salinities. Thermal stability of xanthan strongly depends on salinity. The reported results indicate that xanthan solutions are thermally stable at salinity where xanthan attains an ordered structure. For example, a xanthan solution containing 1g/L NaCl was not thermally stable at 90^{o}C owing to the disordered structure at this salinity. However, a xanthan solution containing 50 g/L NaCl was thermally stable at 90^{o}C due to the formation of an ordered structure at this salinity level (Lund, Lecourtier et al. 1990). This property is highly desirable for EOR applications and it shows the potential application of xanthan flooding in high-salinity reservoirs. In general, xanthan is not stable at high temperatures (> 90^{o}C).

2.2.7.1.2 Rheology of Xanthan Gum

At room temperature, xanthan has non-Newtonian pseudo plastic behavior (Richardson and Ross-Murphy 1987), and in solution xanthan shows shear thinning and the viscosity decreases with shear. Polymers can experience a very high shear during pumping and near the well bore region. Xanthan is more shear resistant when compared to HPAM (Abbas, Donovan et al. 2013),which is attributed to the rigid or rod like structure of xanthan. Viscoelastic behavior of HPAM is due to chain entanglement, and on applying high shear HPAM chains are unable to relax fast and breakage may occur. On the contrary, at high shear rigid rod like chains of xanthan tend to align with the flow field with minimum breakage (Abbas, Donovan et al. 2013). A highly viscous solution is obtained due to the helical conformation and it is stabilized by the formation of hydrogen bonds between the backbone and the side chains(Seright, Seheult et al. 2009; Bejenariu, Popa et al. 2010). At high concentrations xanthan solutions can even form a liquid crystalline phase (Bejenariu, Popa et al. 2010). Adding a small amount of salts to an aqueous solution of xanthan gum decreases the viscosity due to the charge shielding effect (Wang, Wang et al. 2002; Xu, Xu et al. 2012). However, increasing the concentration of salts does not have a significant effect on the viscosity (Xu, Xu et al. 2012). Similarly, the dynamic modulus also decreases with the addition of salts, but further addition of salts has a negligible effect on the dynamic modulus (Xu, Xu et al. 2012). In summary, at high salt concentrations, xanthan shows much better rheological properties compared to HPAM. Moreover, shear resistance is also better compared to HPAM.

2.2.7.1.3 Adsorption of xanthan gum

Adsorption of xanthan gum on limestone is mainly due the electrostatic attraction between the positively charged limestone surface and the negatively charged pyruvate functional group. One of the most important factors determining the adsorption of xanthan is pH. Adsorption is high when the pH is below 8.2 and decreases as the pH increases above 8.2 due to the negative charge induced on the limestone rock surface. Another mechanism responsible for the adsorption of xanthan gum is salting out at high salinity. Saltsmay increase or decrease the adsorption of xanthan gum, and above the plateau region, adsorption of xanthan gum increases by the addition of salt and vice versa (Celik, Ahmad et al. 1991). This is due to the competing effects of salting-out and electrostatic attraction. Increasing the temperature, which causes coiling of xanthan gum, helps in the reduction of xanthan adsorption on limestone due to lesser exposure of negative side chains of coiled xanthan to rock surfaces(Celik, Ahmad et al. 1991). In the presence of surfactants, the adsorption of the polymer competes with the adsorption of the surfactant. Adsorption in the presence of ethoxylated sulfonate was studied by Celik et al. (Celik, Ahmad et al. 1991), andas both the polymer and the surfactant carry negative charges, a competition exists between the ethoxylated surfactant and the xanthan polymer. Data from Celik et al. show that surfactant adsorption is much faster when compared to the polymer due to low molecule size of the surfactants. Adsorption of xanthan gum on sand was found to increase by the addition of calcium (Lee, Lecourtier et al.),and the adsorption is controlled by the competition of electrostatic repulsion and hydrogen bonding between xanthan and mineral surfaces. Although at low ionic strengths electrostatic repulsion dominates and adsorption is low, at high ionic strength

electrostatic repulsion decreases which leads to an increase in the adsorption (Lee, Lecourtier et al.). In summary, adsorption of xanthan gum is low when compared to the adsorption of HPAM (Lee, Lecourtier et al.)

2.2.7.1.4 Problems Associated with Xanthan Gum

Main problems associated with xanthan gum are high cost, viscosity loss due to biochemical reactions, biodegradation, and infectivity issues due to cellular debris that may remain after manufacturing (Wellington 1983; Taylor and Nasr-El-Din 1998; Rashidi, Blokhus et al. 2010; Rashidi, Blokhus et al. 2011). Xanthan gum is not suitable for reservoirs with temperatures above 93^{o}C (Doe, Moradi-Araghi et al. 1987). Aqueous solutions of xanthan gum has a low elasticity (Xu, Xu et al. 2012), and the bacterial degradation of xanthan gum can be reduced with formaldehyde under field conditions(Abbas, Donovan et al. 2013).

2.2.7.2 Other Biopolymers

Laboratory evaluation of some other natural biopolymers is reported in the literature for cEOR applications. Scleroglucan is a type of non-ionic polysaccharide obtained by the fermentation of the pathogen fungus genus *Sclerotium*. Repeating unit of scleroglucan is shown in the Figure 2-8.The non-ionic nature of the polymer makes it salt resistant, and it consists of a rod like triple helix structure and in aqueous solution behaves like semi-rigid molecules. Due to the rigidness, viscosity and shear resistance of the polymer is high in aqueous solution (Kulawardana, Koh et al. 2012).The triple helix nature also improves the thermal stability of scleroglucan (Kulawardana, Koh et al. 2012). There is variation among the thermal stability data reported in published studies. While Davison (Davison

and Mentzer 1982) reported that scleroglucan is stable for 500 days at 90^{o}C, Rivenq et al. reports the stability limit as 100^{o}C for 60 days (Rivenq, Donche et al. 1992). Kalpakci et al. (Kalpakci, Jeans et al. 1990) found that scleroglucan was thermally stable for 720 days at 100^{o}C.The major problem hindering the application of scleroglucan is its poor filterability (Kulawardana, Koh et al. 2012).

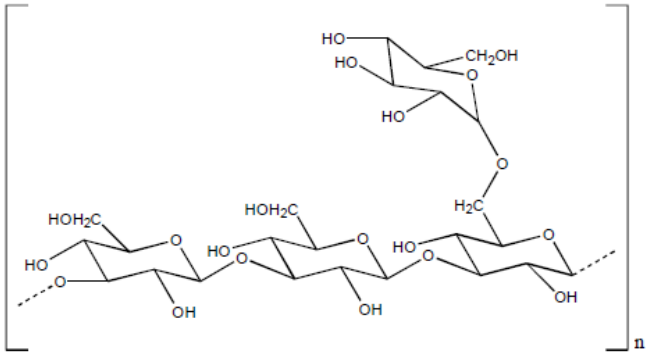

Figure 2-8: Repeating unit of scleroglucan (Kulawardana, Koh et al. 2012)

Another gum in this class is welan gum which is produced by Alcaligenes. Under the same conditions, a high oil recovery was observed for welan gum when compared to xanthan gum. Structure of welan gum is shown in Figure 2-9. Non-ionic and biodegradable polysaccharide guar gum has also been reported in the literature (Wang, Li et al. 2014).

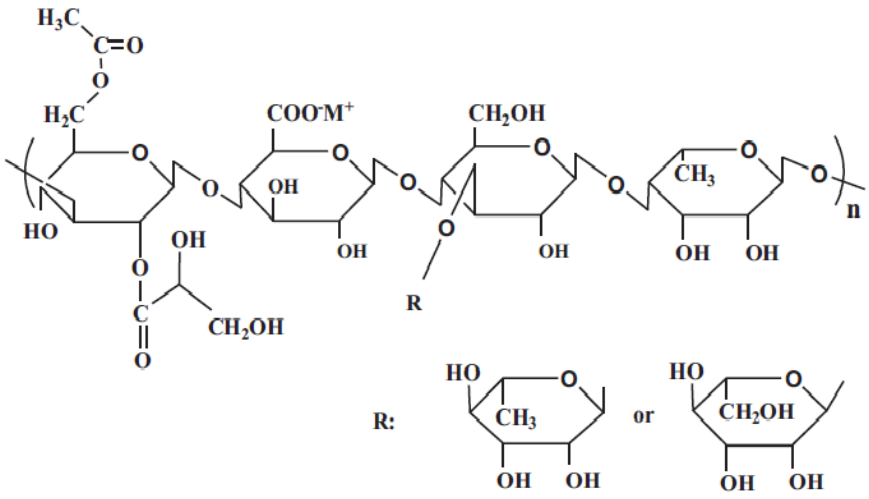

Figure 2-9: Structure of welan gum (Bejenariu, Popa et al. 2010)

Hydroxyethylcellulose (HEC) is an environment friendly nonionic hydrophilic polysaccharide, which is obtained by the chemical modification of water insoluble cellulose. In this modification, cellulose is reacted with ethylene oxide resulting in apendant hydroxyethyl group(Abbas, Donovan et al. 2013). The advantage of the HEC polymer is that it does not have problems associated with cellular debris like xanthan; thus, the HEC polymer does not have any infectivity issues like xanthan(Abbas, Donovan et al. 2013). HEC polymer chains do not have a helical structure like xanthan gum, and therefore the viscosity decreases with temperature (Abbas, Donovan et al. 2013). Thermal stability of HEC strongly depends on pH. While at low pH, the hydrolysis of acetal linkages causes a viscosity reduction, at neutral and high pH hydrolysis rate is reduced significantly.

In another approach, a biopolymer is grafted and copolymerized with synthetic polymers. For example starch-graft-poly (acrylamide-co-2-acrylamido-2- methylpropanesulfoacid) [S-g-P (AM-co-AMPS)] was synthesized based on both natural and synthetic

polymers(Song, Zhang et al. 2007). Better oil recovery was reported compared to HPAM at similar conditions. No further data is available for this type of polymers.

Thermal stability of a range of polymers determined by laboratory evaluation and reported in the literature is summarized in Table 2-3. Data presented in Table 2-3 can be used to select a suitable polymer at varying conditions of temperature and salinity. The number of days indicated in Table 2-3 is the maximum time the polymer was evaluated for thermal stability. However, the polymer can be stable for a longer period of time under similar conditions of salinity and temperature.

Table 2-3: Thermal stability of various polymers under varying conditions

	Salinity (ppm)	**T (^{o}C)**	**Time (days)**	**Comments**	**Ref**
HPAM	30000	85	100	Reference for other polymers	(Levitt and Pope 2008)
HPAM	20000	90	619	-	(Ryles 1988)
AMPS-AM	30000	100	200	Higher cost	(Levitt and Pope 2008)
AMPS-AM	33560	93	100	Higher cost	(Moradi-Araghi, Cleveland et al. 1987)
NaAMPS	33560	121	100	Higher cost	(Moradi-Araghi, Cleveland et al. 1987)
VP-AM	33756	121	100	Lower molecular weight, lower viscosity	(Doe, Moradi-Araghi et al. 1987)
NNDAM-NaAMPS	0	120	30	Higher cost	(Sabhapondit, Borthakur et al. 2003)
AM-CE	10000	60	180	Limited data	(Bai, Za et al. 2012)
AM-AMPS - VN	67, 850	80	90	Lower molecular weight	(Zhong, Luo et al. 2009)
Xanthan Gum	170,000	80	300	Viscosity loss due to biochemical reactions, biodegradation, and injectivity issues	(Han, Yang et al. 1999)
Scleroglucan	30, 000	100	720	Poor filterability	(Kalpakci, Jeans et al. 1990)

2.3 Current Laboratory and Field Work and Future Look

Polymer flooding did not get much attention in the past due to high chemical cost, inadequate understanding of the mechanism, unavailability of efficient chemicals, and low crude prices. Now, PF is attracting researchers around the world due to depletion of oil reserves, high crude oil prices, technological advancements, and the availability of chemicals at relatively low price(Seright 2010; Guo, Dong et al. 2013; Van Wunnik, Stoll et al. 2014). For example, forty years back oil prices were $3/bbl and polymer cost was 1.5/lb USD. However, currently the oil price is around $100/bbl while the polymer prices have remained the same (Pope 2011).As only about 1 to 2 lbs of polymer are required, it will cost only about2 to 3 USD to produce incremental oil of 1 bbl (Pope 2011). Polymer flooding has been implemented worldwide in many oil fields. A list of oil fields where PF has been applied either on a commercial scale or pilot scale is given in Table 2-4. China is the world leader in the implementation of cEOR projects and Daqing is the world's largest oil field where PF has been implemented. Table 2-5 lists the field conditions where PF has been implemented and the type of polymer used. Most of these reservoirs are at relatively low-temperature and low-salinity, and HPAM is the most widely used polymer in the field, mainly in low-temperature and low-salinity reservoirs. For xanthan gum, it is used in some fields with high-salinity and low-temperature reservoirs. The data presented in Tables 2-5 and 2-6 indicate that, although a range of novel polymers have been evaluated on lab scale, field applications are limited to HPAM and xanthan gum. As most of the remaining oil reserves have a higher temperature and higher formation salinity, it is expected that novel polymers currently under laboratory evaluation will replace HPAM. Also, data presented in Table 2-5 show that PF is mainly implemented in

sandstone reservoirs. Due to the fact that most of the remaining oil is in carbonate reservoirs, several laboratory evaluations are underway to extend PF to carbonate reservoirs.

The real challenge for PF is in the extension of its application to HTHS reservoirs. HPAM needs to be injected at a high concentration in HTHS reservoirs due to poor salt tolerance. Other thermally stable and salt tolerant polymers are expensive and not as good viscosities like HPAM. Recently, impact of water softening on economics of cEOR was analyzed and it was found that chemical cost can be decreased significantly by using soft sea water. In addition to high-temperature and high-salinity, low permeability is another hurdle against the use of polymer flooding. The molecular weight of the polymer is the most important factor in deciding the lower limit of permeability (Pope 2011). High molecular weight polymers are attractive but it either can damage the pore space or may not be able to flow through small pores (Wei, Saleh et al. 2014). For low permeability reservoirs, a polymer with a low molecular weight should be used, which have to be injected at a relatively high concentration that will increase the per bbl incremental oil cost. Oil recovery from carbonate reservoirs is more complex when compared to sandstone reservoirs. The carbonate rock surfaces are positively charged at moderate pH, the carboxylic acid present in the core can adsorb on the rock surfaces. Adsorption of carboxylic acid in the core makes the carbonate reservoirs oil wet(Hamouda and Rezaei Gomari 2006). The majority of the carbonate reservoirs are oil wet(Anderson 1986) and the recovery in oil wet media is always lower when compared to water wet media(Sedaghat, Ghazanfari et al. 2013). Another complexity associated with carbonate reservoirs is reservoir heterogeneity. There may be natural fractures in the reservoirs that

are more common in the carbonates (Han, AlSofi et al. 2013). The presence of these fractures results in channeling of the injected slug resulting in poor recovery. Absence of fresh water sources and the limited space on the platforms are additional hurdles for implementing cEOR in offshore reservoirs(Han, Xiang et al. 2006; Amirrudin, Zainal et al. 2014). Moreover, there are operational issues like produced water disposal and working around congested urban plan(Stapel, Riethmuller et al. 2014). In summary, there are still some hurdles like HTHS oil reservoir, low permeability reservoir, fractured carbonate reservoirs, operational issues and different logistic problems in offshore reservoirs. Development of polymers that can tolerate HTHS environment with minimum adsorption and cost can significantly increase the amount of oil produced from cEOR. Moreover, technological advancement can reduce several operational and logistic issues.

Table 2-4: Reported worldwide oil fields where polymer flooding has been either applied commercially or on a pilot scale

Country	Field	Ref
China	Daqing, Gudong, Karamay, Shengli, Liahoe, Xing Long Tai, Xia-er-men, Wangchang, Shuanghe,	(Manrique, Thomas et al. ; Chen, Song et al. 1998; Gu, Yang et al. 1998; He, Song et al. 1998; Zhijian, Yigen et al. 1998; Demin, Jiecheng et al. 1999; Zhang, Wang et al. 1999; Qiao, Gu et al. 2000; Li, Liao et al. 2003; Chang, Zhang et al. 2006; Pu and Xu 2009; Sheng 2010)
USA	North Burbank, West Kiehl, Cambridge Minnelusa, Oklahoma, Tanner, Nowata, Bradford, Tambaredjo	(Manrique, Thomas et al. ; Meyers, Pitts et al. 1992; Jay, Jim et al. 2000; Sami, Faisal et al. 2000; Pitts, Dowling et al. 2006; Manichand, Mogollon et al. 2010)
Brazil	Carmopolis, Buracica, Fz.Focinho, Canto do Amaro, Voador Offshore Field	(Manrique, Thomas et al. ; Shecaira, Branco et al. 2002)
India	Viraj, Sanand , Jhalora	(Mahendra and Gauma 2004; tiwari, Marathe et al. 2008)
Oman	Marmul	(Koning, Mentzer et al. 1988; Al-saadi, Al-amri et al. 2012; Finol, Al-harthy et al. 2012; Jaspers, Al-Amri et al. 2013)
Austria	Matzen	(Kornberger, Gumpenberger et al. 2013)
Argentina	El Tordillo, Diadema	(Manrique, Thomas et al. ; Buciak, Fondevila Sancet et al. 2013)
Canada	Pelican Lake, Horsefly Lake Field, David Pool	(Manrique, Thomas et al. ; MJ>, Wyatt et al. 2004)
Germany	Bochstedt Field, Eddesse-Nord, Vorhop-Knesebeck, Scheerhorn	(Manrique, Thomas et al. ; Abbas, Donovan et al. 2013)
Indonesia	Minas	(Sami, Faisal et al. 2000)
Russia	Russia Romashkino Field	(Loppinet, Iakovlev et al. 1997)

Table 2-5: Some polymers applied in various fields

Field	**Polymer**	**T (^{o}C)**	**Formation Salinity (mg/L)**	**Ref**
Daqing	HPAM	45	9000	(Pu and Xu 2009)
Pelican	HPAM	23	6800	(Mogollon and Lokhandwala 2013)
Gudong	HPAM	68	3022	(Zhijian, Yigen et al. 1998)
Tambaredjo	HPAM	36	Not Specified	(Mogollon and Lokhandwala 2013)
Bohai Bay	HPAM	65	6070	(Mogollon and Lokhandwala 2013)
Henan oil field	HPAM	75	5060	(Chen, Song et al. 1998)
XingLongTai	HPAM	56.6	3112	(Zhang, Wang et al. 1999)
West Khiel	HPAM	57	46,480 (P)[a]	(Meyers, Pitts et al. 1992)
Tanner	PAM	80	66800 (P)[a]	(Pitts, Dowling et al. 2006)
Cambridge Minnelusa	PAM	55.6	Not specified	(Jay, Jim et al. 2000)
Viraj	HPAM	81	13,250	(Mahendra and Gauma 2004)
Sanand	PAM	85	Not specified	(tiwari, Marathe et al. 2008)
Matzen	HPAM	50	20,000	(Kornberger, Gumpenberger et al. 2013)
David pool	PAM	31	6660(I)[b]	(MJ>, Wyatt et al. 2004)
Eddesse-Nord sand stone reservoir	Xanthan	22	120,000	(Abbas, Donovan et al. 2013)
Vorhop-Knesebeck	Xanthan	56	210,000	(Abbas, Donovan et al. 2013)
Romashkino field in Tatarstan (Russia)	HEC	36	250,000	(Loppinet, Iakovlev et al. 1997; Abbas, Donovan et al. 2013)
Bohai oil field	AP-P4	65	32423	(Han, Xiang et al. 2006)

[a]Produced water salinity. [b]Injection water salinity

Table 2-6: Laboratory Core flooding data of some selected polymers

Polymer	Conc[a] (ppm)	T[b] (^{o}C)	Core[c]	Recovery[d] (%)	Ref
Xanthan	500	50	S	66 T	(Austad, Ekrann et al. 1997)
AMPS-AM	1000	50	S	53.6 T	(Austad, Ekrann et al. 1997)
AM- (N-PMI) (5000 ppm)	5000	85	S	8.5	(Liu, Jiang et al. 2012)
NNDAM-NaAMPS	2000	60	S	11	(Sabhapondit, Borthakur et al. 2003)
HPAM	2000	70	S	34	(Gong, Xu et al. 2008)
AM- (*N*-NABI)	7000	60	S	10.6	(Ye, Gou et al. 2013)
HPAM	1100	75	S	9.8	(Chen, Song et al. 1998)
HPAM	2500	45	S	16.7	(Liu, Sun et al. ; Yang, Wang et al.)
HPAM	4500	38	C	45	(Panthi, Mohanty et al.)
AM-(O- β-CD)	2000	60	Not specified[e]	12	(Liu, Jiang et al. 2013)
AM-(A- β-CD)	2000	60	Not specified[e]	18	(Liu, Jiang et al. 2013)
AM-AA-DNDA	2000	65	S	5.7	(Lai, Dong et al. 2012)
TVP	2000	85	S	13.5	(Chen, Wang et al. 2013)

[a]Polymer concentration. [b]Temperature .[c]Core type: sandstone (S), carbonate (C).[d]Recovery reported with T is total recovery while remaining value are additional recovery due to PF.[e]Not indicated in the corresponding article.

2.4 Conclusion

Thermal stability, rheology, adsorption, and field applications of various polymer systems used in polymer flooding for EOR are reviewed. These polymers include: partially hydrolyzed Polyacrylamide, novel copolymers of Polyacrylamide, hydrophobic ally modified associating Polyacrylamide, thermo-viscosifying polymers, cationic polymers, and various biopolymers. Reservoir conditions like temperature, salinity, charges on the rock surfaces, and the nature of crude oil are important parameters of consideration for polymer flooding. HPAM provides good viscosification at comparatively low-temperature and low-salinity. For high-temperature and high-salinity conditions various copolymers of AM like AM-AMPS and AM-VP are suggested in the literature. Hydrophobic ally associating polymers can provide good viscosification due to intermolecular association. Thermo-viscosifying polymers can also yield good results in high-temperature and high-salinity reservoirs. Data collected from various publications clearly indicate that an extensive researches underway to develop novel polymers that can tolerate harsh reservoir conditions. Almost all the research is focused on acryl amide based copolymers, hydrophobic polymers and thermo-viscosifying polymers. Despite the fact that laboratory evaluation has been shifted from HPAM to novel copolymers, HPAM is still the most widely used polymer in the field. It is mainly due to this reason that most polymer flooding projects have been implemented in low-temperature and low-salinity reservoirs. In the future, novel copolymers of AM will certainly replace HPAM when cEOR will be applied to deeper and hotter reservoirs. The main challenges that face polymer flooding are also addressed.

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CHAPTER 3

RHEOLOGICAL STUDY ON ATBS-AM COPOLYMER-SURFACTANT SYSTEM IN HIGH-TEMPERATURE AND HIGH-SALINITY ENVIRONMENT

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Abstract

Experimental studies were conducted to evaluate the rheological properties of surfactant-polymer (SP) system. This SP system consists of a copolymer of acrylamide (AM) and acrylamido tertiary butyl sulfonate (ATBS) and sodium dodecyl sulphate (SDS) surfactant. Effects of surfactant concentration, temperature, polymer concentration and salinity on rheological properties of SP system were investigated by means of oscillation and shear measurements. Comparison with classical partially hydrolyzed polyacrylamide (HPAM) was made. For the same temperature range, the viscosity drop for HPAM was about four times higher than the viscosity drop for ATBS-AM copolymer. In deionized water, viscosity of both polymers and SP systems was very high as compared to viscosity in saline water. Viscosity reduction of ATBS-AM copolymer was higher for salts having divalent cations. The SP system showed precipitation in presence of divalent cations. It worked well with monovalent cations even at relatively high salinities. The addition of 0.1 % surfactant to the polymer resulted in a 60% decrease in the viscosity. Some interfacial rheological experiments were also carried out to investigate the behaviors on the interface between SP solutions and oil. Addition of 0.1 % surfactant showed a 65% decrease in G′ at SP solution-oil interface. SP system consisting of ATBS-AM and SDS showed better performance at high temperature compared to HPAM-SDS system. Due to precipitation, the SP system should be restricted to environment having low divalent cations.

Keywords: rheology; polyacrylamide; salinity; enhanced oil recovery; polymer floodi

3.1 Introduction

In chemical enhanced oil recovery (cEOR), surfactants are used to reduce the interfacial tension between crude oil and water. Polymers are used to improve the mobility ratio by viscosifying displacing fluid. Enhanced viscosity of displacing fluids can increase macroscopic displacement efficiency by overcoming viscous fingering. Recently, some researchers have proved that these polymers not only improve macroscopic displacement efficiency but also microscopic efficiency due to elasticity (Wang, Cheng et al. 2001; Wang, Xia et al. 2001; Xia, Ju et al. 2004; Xia, Wang et al. 2004; Xia, Wang et al. 2007; Kuru 2010; Zhang, Li et al. 2011).

HPAM which is widely used for cEOR applications (Veerabhadrappa, Urbissinova et al. 2011) fails at high-temperature and high-salinity (HTHS) environment. Extensive hydrolysis of amide group at high temperatures may also cause precipitation of hydrolyzed product in the presence of divalent cations. Field applications of available polymers are limited to low-temperature and low-salinity reservoirs. HTHS reservoirs present a major challenge for implementation of cEOR techniques. Incorporation of some thermally stable and salt tolerant co-monomers can enhance the performance of polyacrylamide in HTHS conditions. Recently, synthesized thermoviscosifying polymers (Petit, Karakasyan et al. 2007; Wang, Feng et al. 2010; Liu, Wang et al. 2012; Chen, Wang et al. 2013) showed some positive results in HTHS environment after some preliminary rheological tests.

Three major types of surfactant-polymer interactions may exist depending upon the nature and structure of polymer and surfactant head group. Firstly, attractive forces

between surfactant and polymer may be stronger than mutual forces of surfactant molecule. Secondly, attractive forces among surfactant molecules may be greater than attractive forces between surfactant and polymer. Thirdly, repulsive forces between surfactant and polymer are very high as compared to attractive forces among surfactant molecules (Methemitis, Morcellet et al. 1986) . The system becomes more complex in the presence of oil, co surfactant, alkali and salts. Many approaches have been adopted to understand the interactions between surfactant-polymer systems. These include: surface tension and interfacial tension measurement, rheology, fluorescence spectroscopy, potentiometry, light scattering and conductivity measurement.

There are some reports available in the literature on the rheology of classical HPAM /SDS (Mandal and Ojha 2008) PAM/SDS (Kopperud, Hansen et al. 1998) and hydrophobically modified PAM (HM-PAM)/SDS (Caputo, Selb et al. 2004) system. Addition of the surfactant has no effect on the rheology of the polymer due to non-ionic nature of PAM. Significant effect of surfactant addition has been reported for HPAM and HM-HPAM due to strong interactions between the surfactant and polymer. By addition of 30 mmol/L (0.86%) SDS, about 85% drop in the viscosity of HPAM is reported by Huang et al.(Huai Tian, Yang et al. 2002). SP solution consisting of SDS and vinylpyridine-AM copolymer in 0.1N NaCl solution has about 90% less viscosity than that of the viscosity of the SP solution in deionized water [16]. Temperature also plays important role in surfactant-polymer interactions. For HM-HPAM/SDS system, Nystrom (Kopperud, Hansen et al. 1998) found that the viscosity at 40^{o}C is 80% less than that of viscosity at 10^{o}C.

Rheology study can be used to screen many SP systems for cEOR applications. In addition, interfacial rheology can provide the insight on the interface between SP solution and oil. The objective of this work is to study the influence of salts, temperature and surfactant concentration on rheological properties of SP system consisting of SDS and ATBS-AM copolymer. Some of the results were compared with HPAM

3.2 Experimental

3.2.1 Materials

Copolymer of AM and ATBS (Flopaam An125SH) with a molecular weight of 8 million Dalton and 25% sulfonation degree was obtained from SNF FLOERGER in a powder form. Classical HPAM (Flopaam 3630S) with a molecular weight of 20 million Dalton and 30% hydrolysis degree was obtained from SNF FLOERGER. Sea water was prepared using laboratory grade sodium bicarbonate, sodium sulphate, sodium chloride, calcium chloride and magnesium chloride with a total salinity of 57,638 mg/L (ppm). SDS with 99% purity was obtained from Sigma Aldrich. The oil used in interfacial rheology experiments has a density of 0.8767 g/cm^3.

3.2.2 Preparation of polymer solutions

A polymer solution was prepared by using magnetically driven stirrer. The polymer was added slowly on the shoulder of the vortex formed by deionized water, surfactant solution or salt solution to avoid formation of slubs. As soon as the entire polymer was added the rotor speed was reduced from 300 to 80 rpm to avoid mechanical degradation. Stirring was turned off after 3 hours and the solution was kept at room temperature for the next 48 hours for complete hydration.

3.2.3 Rheological measurements

Rheological measurements were carried out using discovery hybrid rheometer (DHR-3) from TA Instrument. Concentric cylinder geometry was used to measure both steady state and oscillation measurements. The range of shear rate for steady shear viscosity measurements was from 0.01 to 1000 s^{-1}. Frequency from 0.1 to 100 rad/s was applied for oscillatory measurements. All reported data points are within torque limits (+/- 5mN.m-2000nN.m). Frequency sweep experiments were conducted in the linear viscoelastic region. Oscillation time experiment was performed to check the thermal stability of HPAM and ATBS-AM copolymer. Interfacial rheology experiments were performed using AR-G2 platinum double wall ring interfacial geometry. Frequency was kept at 1 rad /s in oscillation time and temperature ramp experiments unless it is stated otherwise.

3.3 Results and discussion

3.3.1 Effect of surfactant concentration

Copolymer concentration was fixed to 0.25% for experiments with varying surfactant concentration. Unless otherwise specified, the term copolymer in this discussion refers to ATBS-AM copolymer. Figure 3-1 shows the viscosity versus shear rate plots of 0.25 % copolymer in deionized water for different concentrations of surfactant. It is evident from Figure 3-1 that by increasing the surfactant concentration steady viscosity is decreasing. The viscosity of the SP system is low compared to the viscosity of copolymer. By adding 0.3 % surfactant, the viscosity is 80% less than that of the viscosity of the copolymer. Similar degree of viscosity drop by adding SDS has been reported for HPAM (Huai Tian, Yang et al. 2002; Mandal and Ojha 2008). This decrease in viscosity by the addition of

surfactant is due to charge shielding mechanism as reported by Mandal et al. (Mandal and Ojha 2008)for HPAM. At very high shear rate, viscosity is almost the same for all surfactant concentrations due to the dominance of the effect of shear in comparison to charge interactions. Variation of complex viscosity at a frequency of 0.1 rad/s is also shown in Figure 3-2. Storage modulus, G′, versus surfactant concentration is shown in Figure 3-3. G′ decreases with the increase in surfactant concentration. As G′ is a measure of elastic nature, it is obvious that addition of surfactant is causing loss in network structure of ATBS-AM copolymer. Interfacial rheological properties were also evaluated at oil/SP solution interface to examine the influence of surfactant concentration. Figure 3-4 shows the interfacial storage modulus (G_I') versus frequency curves at different surfactant concentrations. At all frequencies, G_I' decreases by increasing surfactant concentration. We can conclude that addition of surfactant is weakening the interface between oil and SP solution. Time sweep measurements were also carried out to determine G_I'. These measurements were performed for 5 minutes and within experimental time no change in storage modulus was observed. Results of time sweep experiment are shown in Figure 3-5. A major drop in G_I' due to addition of 0.1% surfactant is observed, while, further addition of the surfactant has little effect.

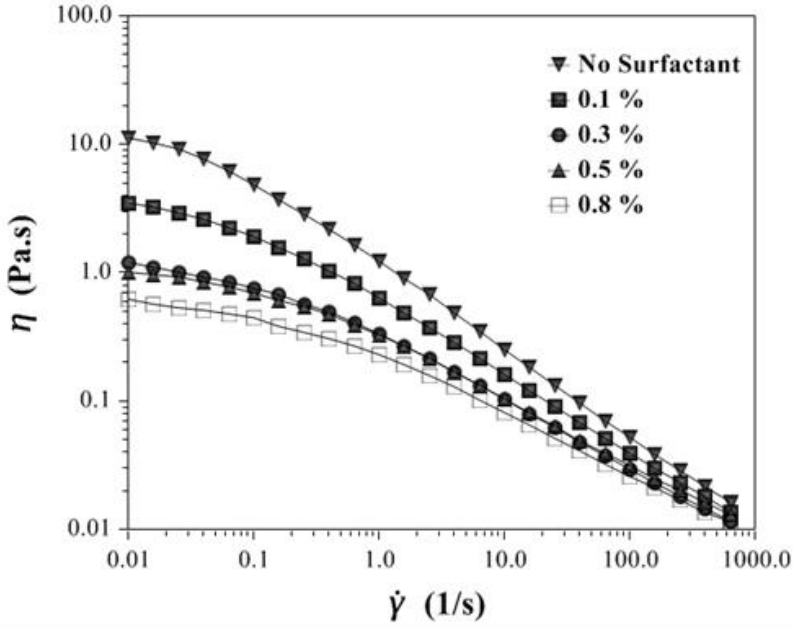

Figure 3-1: Effect of surfactant concentration on steady shear viscosity of copolymer at different shear rates in deionized water at 50^{o}C.

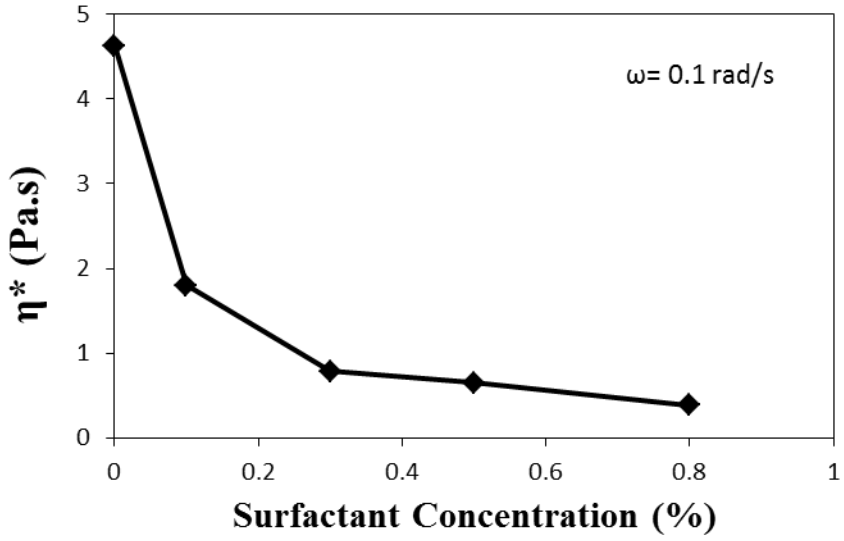

Figure 3-2: Effect of surfactant concentration on complex viscosity of copolymer in deionized water at 50^{o}C.

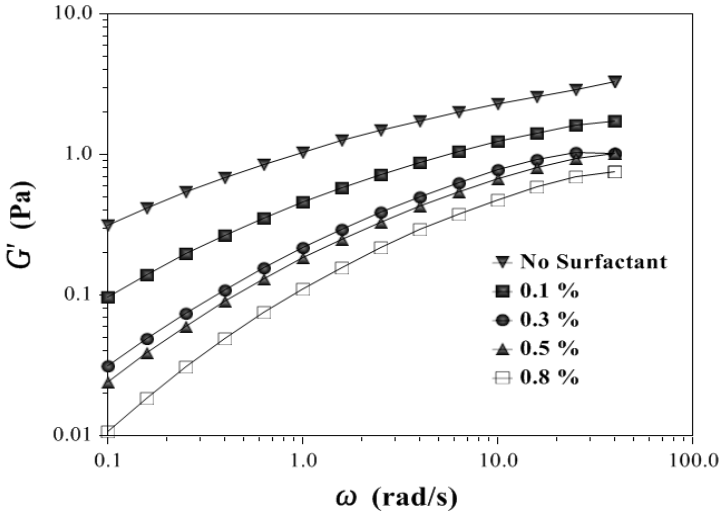

Figure 3-3: Effect of surfactant concentration on storage modulus of copolymer at different frequencies in deionized water at 50^{o}C.

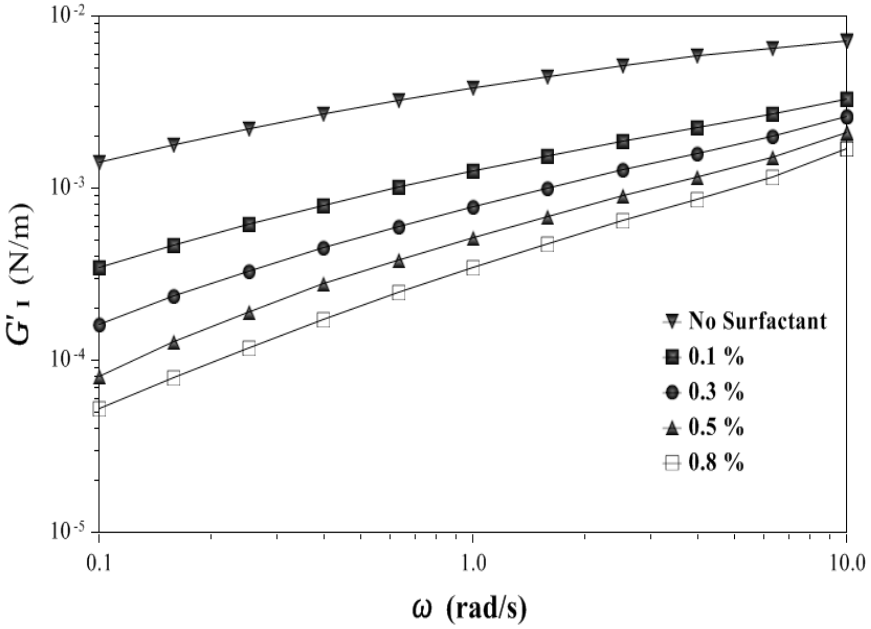

Figure 3-4: Effect of surfactant concentration on interfacial storage modulus of copolymer at different frequencies in deionized water at 25^{o}C

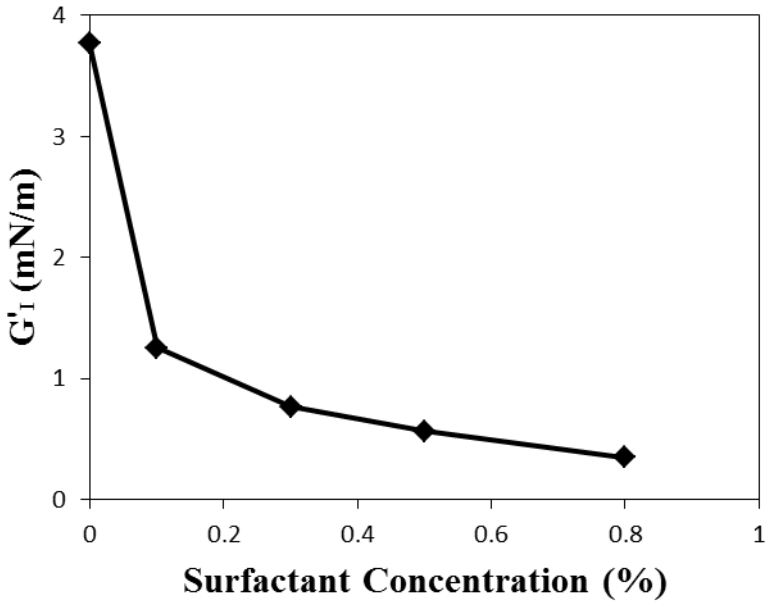

Figure 3-5: Effect of surfactant concentration on interfacial storage modulus of copolymer in deionized water at 25^{o}C.

3.3.2 Effect of temperature

Viscosity versus shear rate plots for HPAM and ATBS-AM copolymer in the absence of surfactant is obtained at two different temperatures (Figure 3-6). It is evident that increasing temperature from 50^{o}C to 90^{o}C causes a major drop in steady shear viscosity of HPAM as compared to the copolymer. At low shear rate, the viscosity of HPAM at 90^{o}C is about 60 % less than its viscosity at 50^{o}C. However, for ATBS-AM copolymer, small change in viscosity (15%) was observed in the same temperature range. This suggests that the viscosity of ATBS-AM copolymer is less sensitive to temperature in comparison with HPAM. Time sweep experiments were run for two hours for both polymers at 50^{o}C and 90^{o}C and results are shown in Figure 3-7. Both polymers were stable at 50^{o}C within the experimental time. Within the experimental time, G′ and

viscosity (not shown) did not change for both polymers. At 90^{o}C, completely different results were found. Unlike ATBS-AM copolymer a continuous decrease in storage modulus of HPAM was observed as experiment proceeds. From the above results it can be concluded that at 50^{o}C both polymers show good stability and can be used at this temperature. However, at 90^{o}C HPAM shows a continuous decrease in rheological properties while AM-ATBS copolymer is stable.

Figures 3-8 and 3-9 present results of temperature ramp experiments at 2^{o}C/min for different surfactant concentrations. Viscosity versus temperature plots are shown in Figure 3-8. At all temperatures, the viscosity of the polymer and SP solutions is decreasing with increasing surfactant concentrations. However, the decrease in viscosity depends on the concentration of surfactant. With no surfactant added in the solution, 20% decrease in viscosity was observed in the temperature range 30^{o}C to 85^{o}C. With the addition of 0.1% surfactant, the viscosity decreases by 33% for the same temperature range. For 0.3% and higher surfactant concentrations about 58 % drop in viscosity was observed. For HM-HPAM/SDS system 80% viscosity decrease was observed when temperature was increased from 10 to 40^{o}C (Kopperud, Hansen et al. 1998). This shows that ATBS-AM /SDS system perform much better in high temperature compared to HM-HPAM/SDS system. Arrhenius model was used to obtain activation energy of viscous flow and pre-exponential factor for solution of different surfactant concentrations. Activation energy of viscous flow increased while pre-exponential factor decreased with the addition of surfactant (Table 3-1). The percentage decrease in the pre-exponential factor is high as compared to the percentage increase in the activation energy. The above data indicate that in the presence of a surfactant, temperature has more effect on the

viscosity of SP solutions as compared to copolymer solution having no surfactant. Similarly, for polymer solution without surfactant, a 26 % drop in G′ was noted. For 0.3% and higher surfactant concentrations about 70% decrease in storage modulus was observed in the same temperature range. Effect of temperature on G_I' is shown in Figure 3-10. With the increase in temperature G_I' also decreases. This shows that temperature is also weakening the interface but its effect is not as much when we compare it to the effect of surfactant concentrations. The surfactant concentration is a major source of reduction in interfacial rheological properties between SP solution and oil interface.

Table 3-1: Activation Energy, pre-exponential factors obtained from Arrhenius model for different surfactant concentrations**.**

Concentration (%)	Ea[a] (kJ/mole)	A[b] (mPa.s)
0	5.020	210.74
0.1	7.010	45.177
0.3	14.54	1.2797
0.5	15.38	0.8152
0.8	15.877	0.5497

[a] Ea is activation energy of viscous flow [b] A is pre-exponential factor

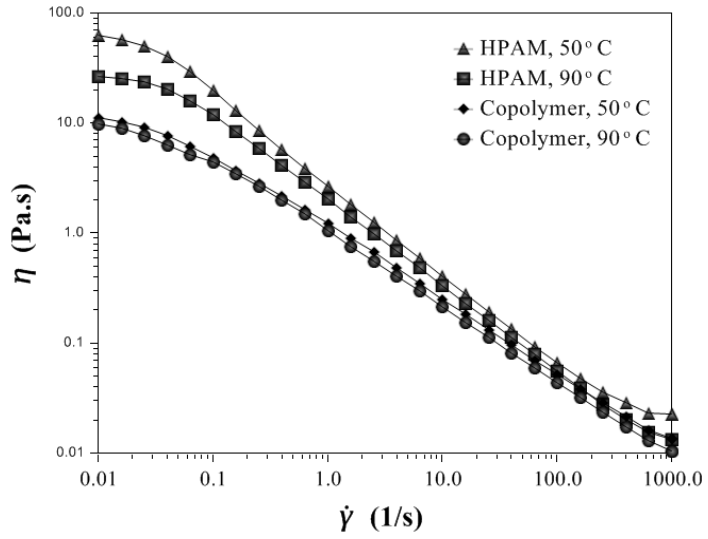

Figure 3-6: Steady shear viscosity profile of HPAM and ATBS-AM copolymer solutions in salt-free water without surfactant at 0.25% polymer concentration.

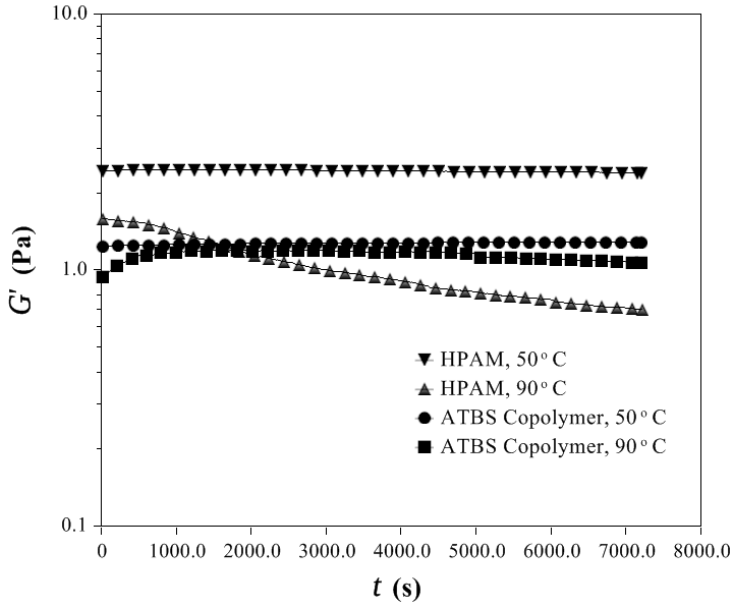

Figure 3-7: Comparison of G'of HPAM and ATBS-AM copolymer solutions in deionized water by time sweep measurements at 0.25% polymer concentration.

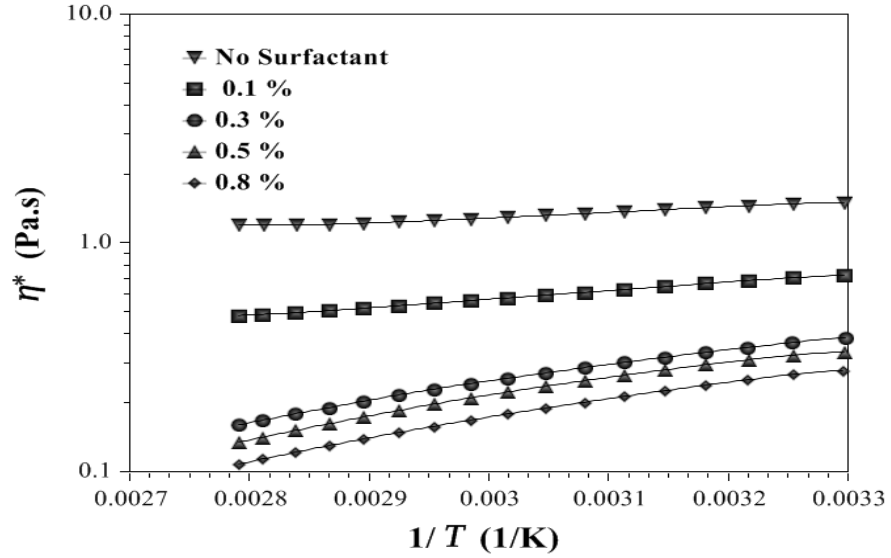

Figure 3-8: Effect of temperature on viscosity of 0.25 % copolymer at different surfactant concentration.

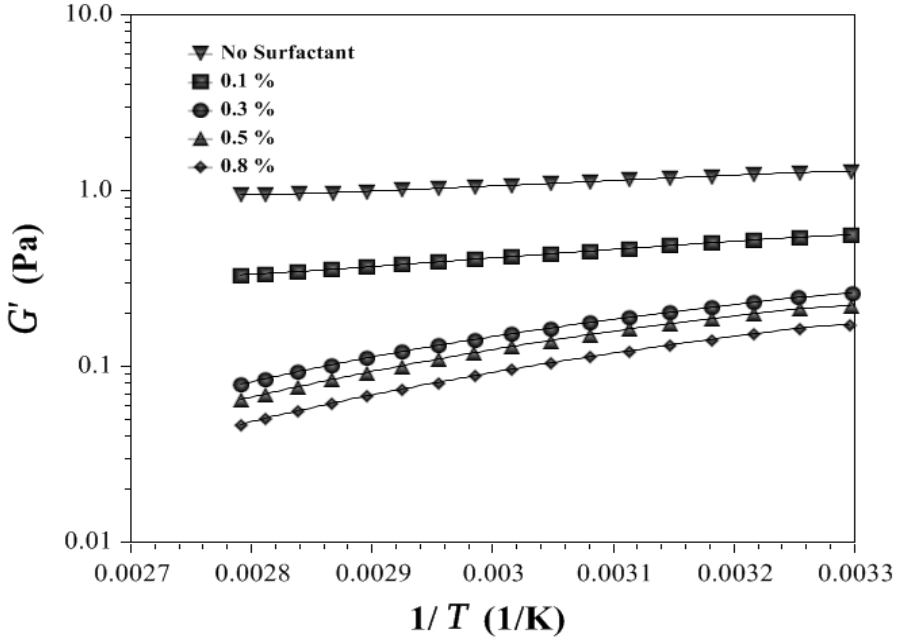

Figure 3-9: Effect of temperature on G' of 0.25 % copolymer at different surfactant concentration.

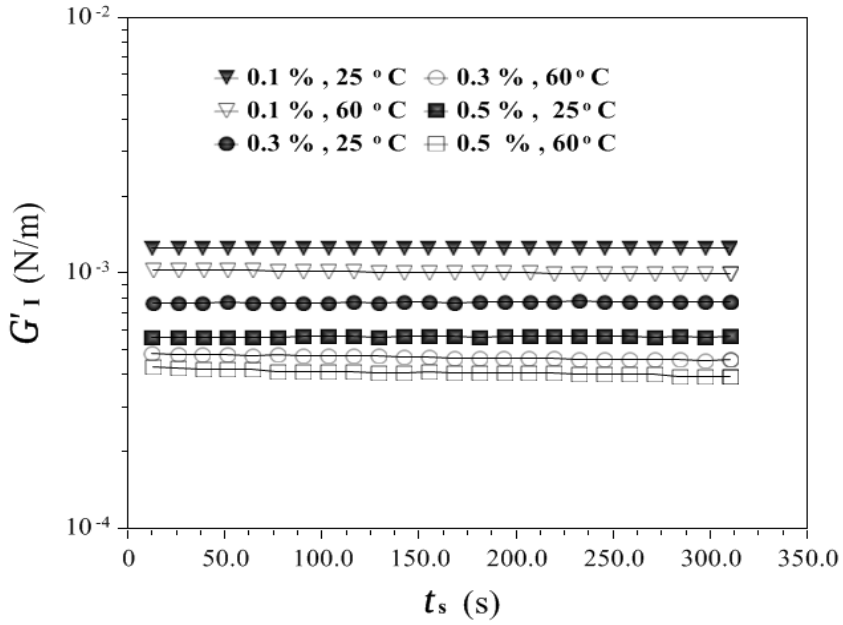

Figure 3-10: Effect of temperature on G_I'of 0.25% copolymer at different surfactant concentration.

3.3.3 Effect of polymer concentration

Surfactant concentration was fixed to 0.3% for all experiments and polymer concentration was varied from 0.1 to 0.4%. Figures 3-11 and 3-12 summarize the effect of polymer concentration on SP system. No unusual results were observed by changing the polymer concentration. It is clear from Figures 3-11 and 3-12 that increasing the concentration of polymer will cause increase in steady shear viscosity. This increase is more prominent at low shear rate. Results of temperature ramp experiments at a rate of 2^oC/min for different copolymer concentrations are shown in the Figures 3-13 and 3-14. Both storage modulus and viscosity decrease with increasing in temperature at all polymer concentration. However, the decrease in the viscosity and storage modulus depends on the polymer concentration. Maximum drop in viscosity (58 %) and storage

modulus (70%) was found for SP solution having minimum polymer concentration (0.15%) and minimum drop in viscosity (49%) and storage modulus (57%) was found with SP solution of highest polymer concentration (0.4%). Activation energy of viscous flow and pre-exponent factors for SP solutions of different polymer concentrations were calculated and tabulated in Table 3-2. Pre-exponent factor and activation energy of viscous flow of the SP solutions don't change significantly by changing the polymer concentration. However, slight change in surfactant concentration significantly changes the pre-exponent factor and activation energy of the SP solutions. Decrease in the viscosity with temperature depends mainly on surfactant concentration and polymer concentration has little effect.

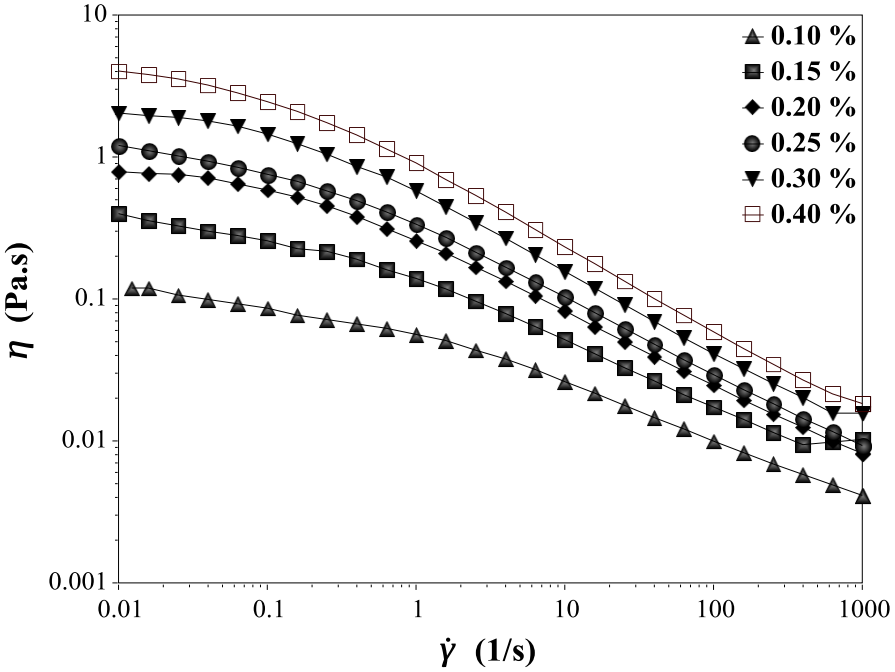

Figure 3-11: Steady state viscosity profile of SP solutions with varying concentration of copolymer at 50^{o}C.

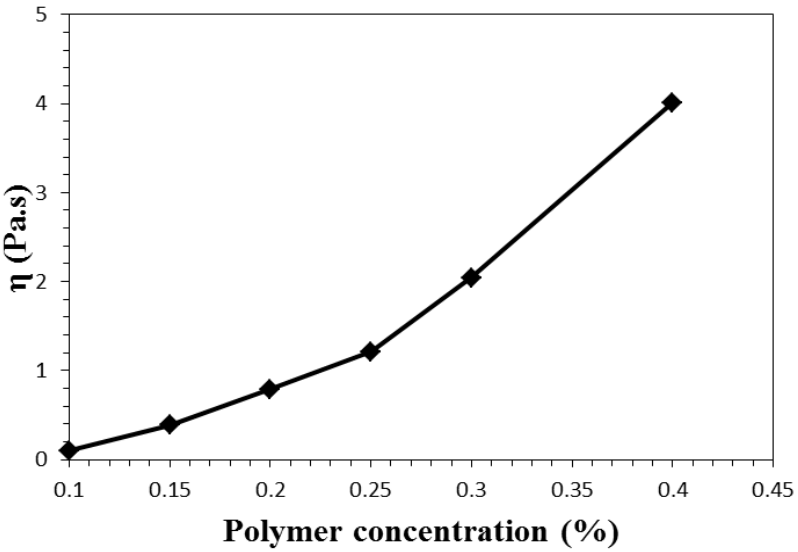

Figure 3-12: Effect of copolymer concentration on viscosity of SP solution at 50^{o}C and shear rate of 0.01 s^{-1}.

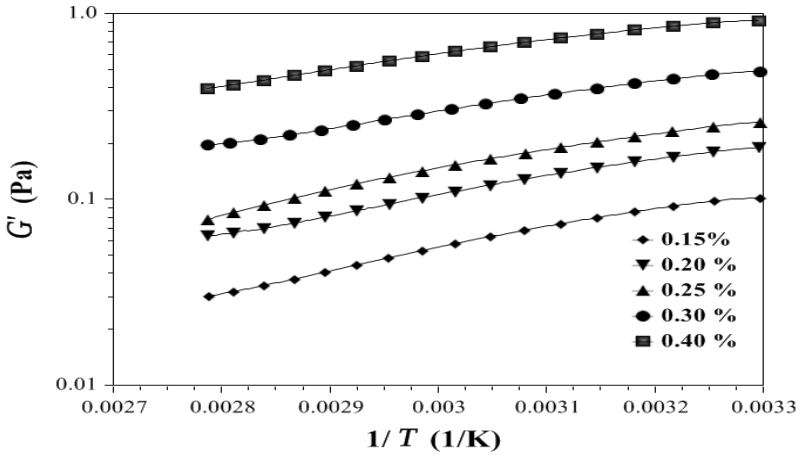

Figure 3-13: Effect of copolymer concentration on storage modulus of SP solution at different temperatures**.**

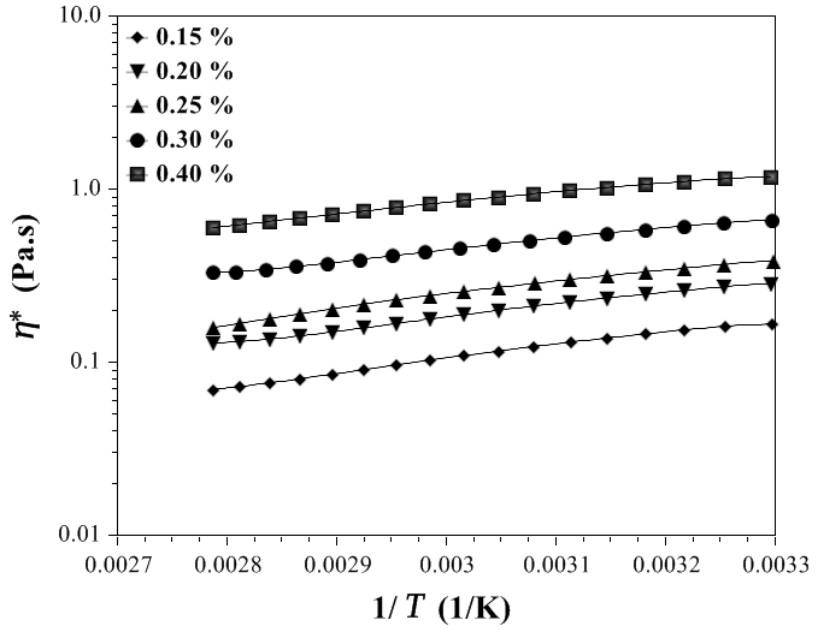

Figure 3-14: Effect of copolymer concentration on viscosity of SP solutions at different temperatures.

Table 3-2: Activation Energy and pre-exponential factors obtained from Arrhenius-type Relation for different polymer concentrations**.**

Concentration (%)	Ea[a] (kJ/mole)	A[b] (mPa.s)
0.15	18.32	0.4266
0.20	16.94	1.1205
0.25	14.54	1.2797
0.30	14.90	5.0728
0.40	13.86	12.891

[a] Ea is activation energy of viscous flow [b] A is pre-exponential factor

3.3.4 Effect of salts

High temperatures and high salinities are real challenges for polymer flooding for the Middle East carbonate reservoirs. In the presence of salts and higher temperatures, viscosity of HPAM decreases. Synthetic sea water with a total salinity of 57638 mg/L containing 2732 mg/L divalent cations was prepared in the lab. It is important to see the effect of each individual ion on the SP system used for chemical flooding. Besides sea water salt solutions of NaCl, Na_2SO_4, $MgCl_2$ and $CaCl_2$ were prepared with different molarities. SP solutions of 0.25 % polymer and 0.3 % surfactant concentration were used to evaluate the performance in different salts. Figure 3-15 shows the comparison of viscosity of both polymers in deionized water at 50^oC without a surfactant. A major reduction in viscosity was observed for both polymers by adding synthetic sea water. Figures 3-16 and 3-17 show the effect of sodium chloride concentration on rheological properties of SP system. Steady shear viscosity reduces as the concentration of sodium chloride is increased. Viscosity at zero shear decreases with the increase NaCl concentration. Similar trend was also observed for storage modulus. Addition of salts brings counterions in the system which reduces the stretching in polymer chains by charge screening and resulting in reduction in viscosity and storage modulus. A reduction in viscosity was also observed for sodium sulphate as shown in Figure 3-18. With calcium chloride and magnesium chloride precipitation of SP system was observed. With sea water there was also precipitation but dilution of sea water to 25% sea water and 75% DW gives a clear solution. This observation shows that this SP system should be limited to environment having low divalent cations. In the absence of divalent cations this SP system can be used even at high salinities. Figure 3-19 presents a comparison of the

impact of different counterions on the steady shear viscosity of copolymer. Compared to deionized water, viscosity of polymer is lower in 0.01 M NaCl solution. But this viscosity is still higher than that of SP solution in 0.01M NaCl having a surfactant. Both surfactant and salts are bringing counterions. System having surfactant has more counterions and introducing additional chain collapse. It is also clear from the Figure 3-19 that decrease in viscosity is higher for polymer solution having calcium ions as compared to monovalent sodium ions. Di-valency is the major cause of reduction in viscosity.

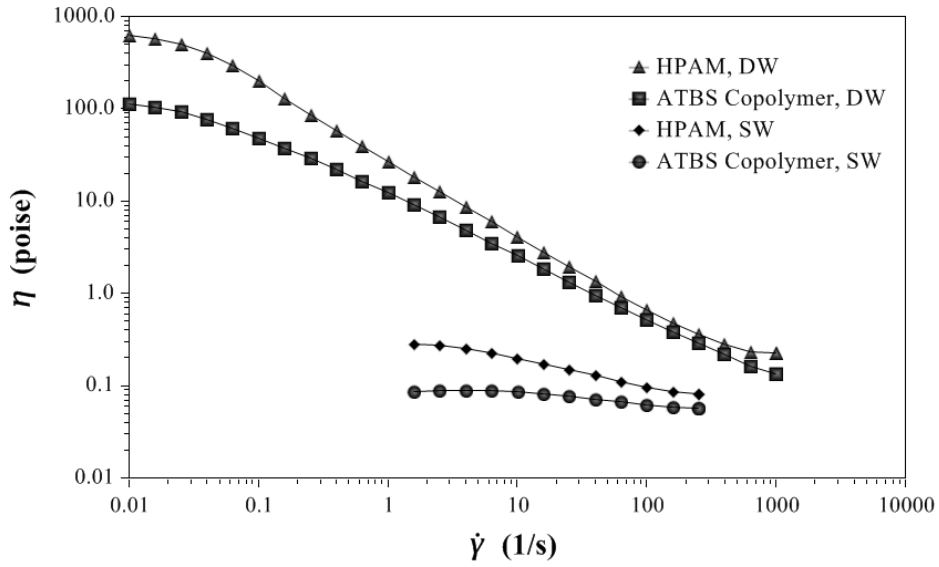

Figure 3-15: Effect of sea water on steady shear viscosity of HPAM and ATBS-AM copolymer without any surfactant at 50^{o}C.

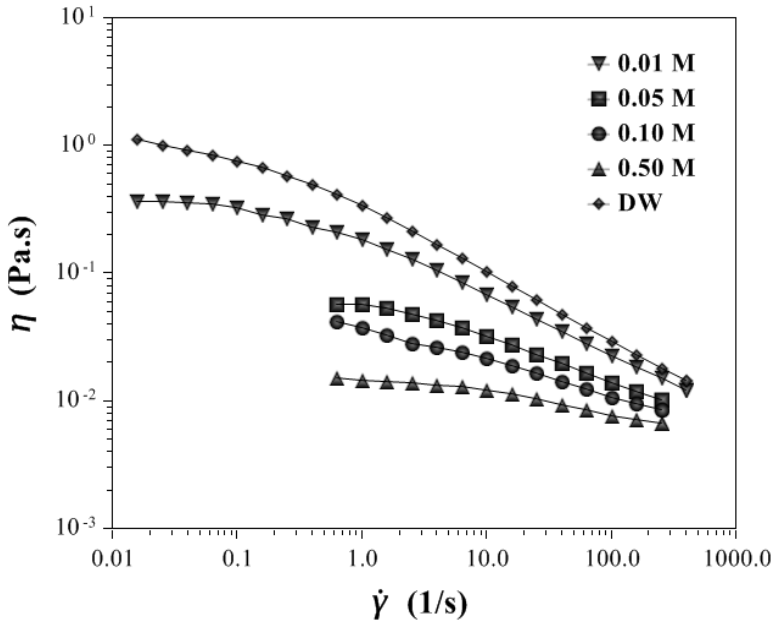

Figure 3-16: Effect of sodium chloride concentration on steady shear viscosity of copolymer at 50^{o}C.

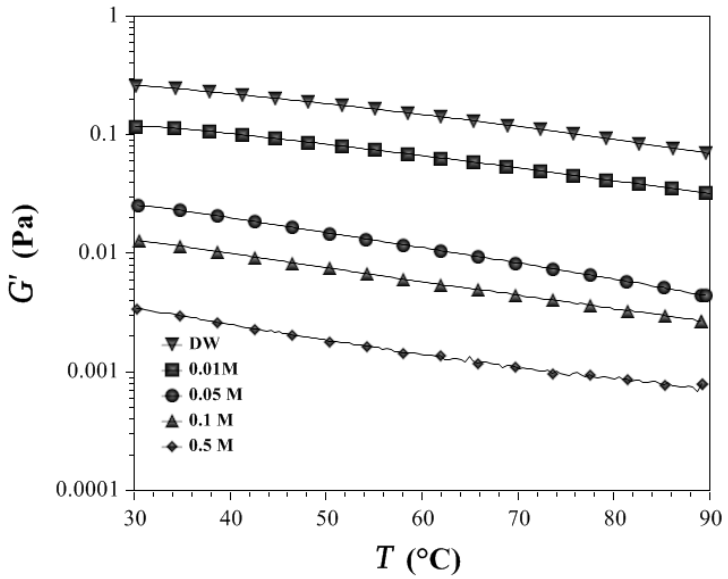

Figure 3-17: Effect of sodium chloride concentration on storage modulus of copolymer at different temperatures.

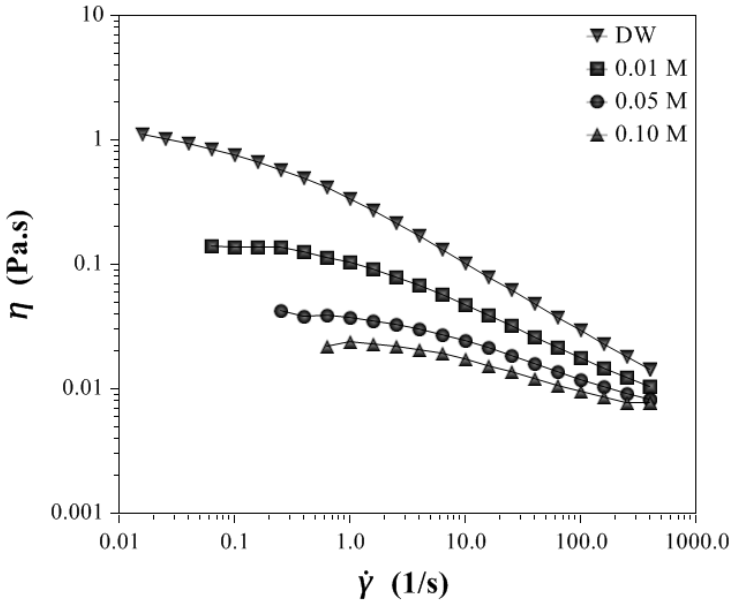

Figure 3-18: Effect of sodium sulphate concentration on steady shear viscosity of copolymer at 50°C.

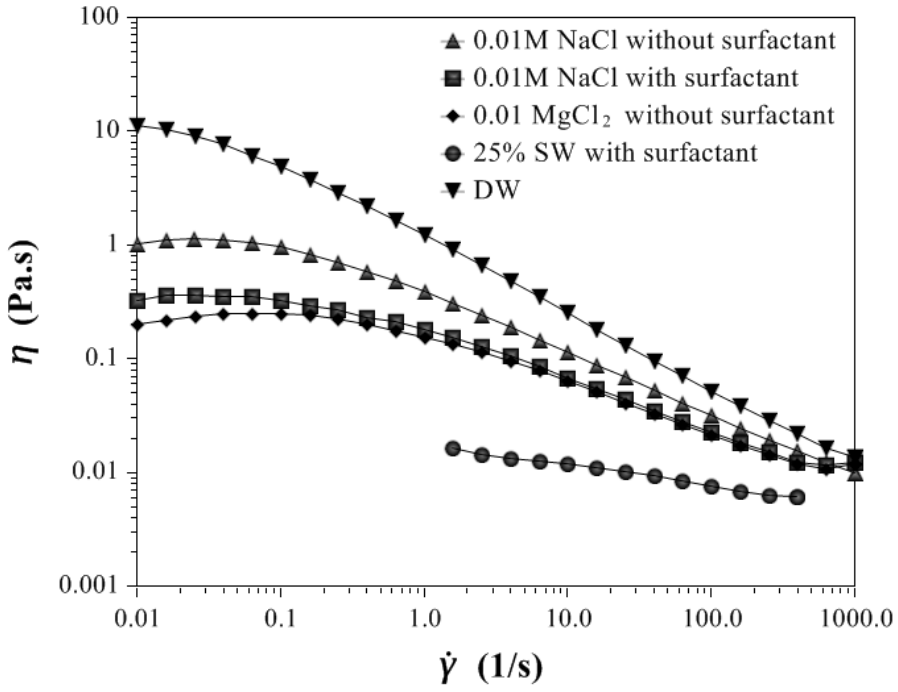

Figure 3-19: Effect of different salt on steady shear viscosity of copolymer at 50°C.

3.4 Conclusions

About 60% reduction in viscosity for HPAM was observed by increasing temperature from 50^{o}C to 90^{o}C. However, decrease in viscosity for ATBS-AM copolymer was 15% for the same temperature range. It can be seen from temperature sweep experiments that at 90^{o}C there was a continuous decrease of storage modulus of HPAM. Copolymer didn't show significant decrease in storage modulus and viscosity within the experimental time. Copolymer of acrylamide and acrylamido tertiary butyl sulfonate (ATBS) has better performance at higher temperatures as compared to partially hydrolyzed polyacrylamide. SP system consisting of AM-ATBS copolymer and SDS showed better performance from rheological point of view at high temperature compared to previously reported HPAM/SDS system. Presence of anionic surfactant SDS is also a source of reduction in the viscosity and storage modulus of polymer solution. Interfacial rheology experiments showed that this surfactant is significantly weakening the interface between SP solution and oil. Effect of each salt on the rheological properties of SP solution was investigated. There is a decrease in the viscosity in the presence of monovalent cations. In the presence of divalent cations precipitation was observed. There was precipitation with sea water. Dilution of this sea water by a ratio of 1:3 with DW yields a solution with no precipitation. Both polymers can be potential candidate for low temperature and low salinity reservoirs. HPAM is not suitable for high temperature reservoirs while ATBS based copolymer can be a potential candidate for high temperature reservoirs.

3.5 Acknowledgements

This research is supported by Saudi Aramco through project # CPM 2297. Authors would like to thank King Fahd University of Petroleum & Minerals (KFUPM) for supporting this research. SNF is also acknowledged for providing polymer samples.

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CHAPTER 4

EVALUATION OF RHEOLOGICAL AND THERMAL PROPERTIES OF A NEW FLUOROCARBON SURFACTANT-POLYMER SYSTEM FOR EOR APPLICATIONS IN HIGH-TEMPERATURE AND HIGH-SALINITY OIL RESERVOIRS

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Abstract

Thermal stability and rheological properties of a novel surfactant-polymer system containing non-ionic ethoxylatedfluorocarbon surfactant was evaluated. A copolymer of acrylamide (AM) and2-acrylamido-2-methylpropanesulfonic acid (AMPS) was used. Thermal stability and surfactant structural changes after aging at 100^{o}C were evaluated using TGA, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and FTIR. The surfactant was compatible with AM-AMPS copolymer and synthetic sea water. No precipitation of surfactant was observed in sea water. The surfactant was found to be thermally stable at 100^{o}C and no structural changes were detected after exposure to this temperature. Rheological properties of the surfactant-polymer (SP) system were measured in a high pressure rheometer. Effect of surfactant concentration, temperature, polymer concentration and salinity on rheological properties was studied for several SP solutions. At low temperature (50^{o}C), the viscosity initially increased slightly with the addition of the surfactant, then decreased at high surfactant concentration. At high temperature (90^{o}C), the increase in the viscosity with the increase in surfactant concentration was not observed. Overall, the influence of the fluorocarbon surfactant on the viscosity of SP system was weak particularly at high temperature and high shear rate. Salts present in sea water reduced the viscosity of the polymer due to charge shielding effect. However, the surfactant was found to be thermally stable in the presence of salts.

Keywords: Fluorocarbon surfactant; Polyacrylamide; Salinity; Enhanced oil recovery.

Polymer floo

4.1 Introduction

About 2,000 billion barrels of conventional oil and 5,000 billion barrels of heavy oil will remain in the reservoirs after applying conventional oil recovery methods like water flooding (Thomas 2007; Wu, Mahmoudkhani et al. 2012). To recover this major fraction of the remaining oil, enhanced oil recovery (EOR) methods are required. Many considerations like oil and rock properties, economic feasibility, technology and availability of raw materials decide the suitable EOR method for a particular reservoir. Chemical EOR (cEOR), thermal EOR and gas flooding are the most popular EOR methods used for recovering additional oil under different reservoir conditions. In cEOR, surfactant (S), polymer (P), alkali (A) or a combination of these chemicals is used. The surfactant reduces the interfacial tension between oil and water while the polymer modifies the rheology of flooding water by increasing its viscosity. Alkalis are used for adjusting the pH to minimize surfactant's adsorption. Alkalis also react with oil, leading to in situ generation of surfactants.

Water soluble partially hydrolyzed polyacrylamide (HPAM) is widely used in cEOR applications. HPAM is the first choice among the available water soluble polymers for cEOR applications due to many desirable properties such as large hydrodynamic volume in water and easy to form hydrogen bond with water molecules(Wu, Mahmoudkhani et al. 2012). HPAM works well in low-salinity low-temperature reservoirs but it is highly unsuitable for high-temperature high-salinity (HTHS) environments (Sabhapondit, Borthakur et al. 2003; Levitt, Jackson et al. 2006; Levitt and Pope 2008). HPAM chain is highly flexible and at HTHS it starts folding resulting in a huge decrease in the viscosity. Polymer interactions with salts and

surfactant at high salinity may cause phase separation. Hydrolysis at high temperature may occur and interaction of the hydrolyzed products with divalent cations will lead to polymer's precipitation (Moawad, Elhomadhi et al. 2007; Wang, Feng et al. 2010; Kulawardana, Koh et al. 2012).Replacing some of the acrylate monomer by other monomers showing lower sensitivity to cation shielding, shear and chemical alteration can enhance the thermal stability of the polymer. 2-acrylamido-2-methylpropanesulfonic acid (AMPS) when copolymerized with acrylamide can improve the resistance to cation shielding and precipitation. Some copolymers (Parker and Lezzi 1993; Petit, Karakasyan et al. 2007; Zhong, Luo et al. 2009; Wang, Lu et al. 2011; Liu, Wang et al. 2012; Zaitoun, Makakou et al. 2012; Chen, Wang et al. 2013; Ye, Gou et al. 2013) have been developed at laboratory scale that can tolerate high temperature and salinity but HTHS reservoirs are still a big challenge for cEOR.

Surfactants are the second important component of SP flooding. Fluorocarbon surfactants are surfactants in which at least one hydrogen atom of the hydrophobic part of the surfactant is replaced by a fluorine atom. Exceptionally low surface tension at small concentrations is the major characteristic of fluorocarbon surfactants (Shinoda, Hato et al. 1972; Abe 1999; Zhang, Shi et al. 2013). Moreover, cationic, anionic, amphoteric and non-ionic fluorocarbon surfactants are available (Murphy and Hewat 2008). Bond between carbon and fluorine is a strongest bond which enhances the stability of fluorocarbon surfactants. It has been proven that adsorption of non-ionic surfactants on calcite is very small compared to anionic surfactants(Sheng 2010). Considering the above mentioned properties, a non-ionic ethoxylated fluorocarbon surfactant was selected for evaluation in combination with an AMPS-AM copolymer at HTHS conditions.

Efficacy of non-ionic fluorocarbon surfactants as materials to displace oil from reservoir rock surface has not been studied extensively. Limited data is available on the application of non-ionic fluorocarbon surfactants in flooding studies. Interactions between AMPS–AM copolymer and the fluorocarbon surfactant were not investigated before. In this work, thermal stability of non-ionic fluorocarbon surfactant has been studied by FTIR, NMR and TGA. Interactions between surfactant and polymer were investigated by rheological techniques. Both steady and dynamic rheological properties were measured. Major parameters covered in this study were surfactant concentration, polymer concentration, temperature and nature of counter-ions.

4.2 Experimental

4.2.1 Materials

AM-AMPS copolymer, Flopaam An125SH, with a molecular weight of 8 million Dalton and 25mole %sulfonation was obtained in powder form from SNF FLOERGER. Sea water was prepared using laboratory grade sodium bicarbonate, sodium sulphate, sodium chloride, calcium chloride and magnesium chloride with a total salinity of 57,638 ppm. Non-ionic ethoxylated fluorocarbon surfactantCapstone®FS-31was obtained from DuPont.

4.2.2 Preparation of Polymer Samples

Magnetically driven stirrer was used to prepare polymer solutions at room temperature. Polymer was added slowly on the shoulder of a vortex formed by deionized water, surfactant solution or salt solution to avoid formation of slobs. After addition of polymer, the rotor speed was setto 80 rpm in order to avoid any mechanical degradation of polymer. The solution was kept under this stirring speed for three hours. In order to assure proper hydration, the solution was kept at room

temperature without stirring for another 48 hours. Finally, the solution was diluted to the desired concentration.

4.2.3 Thermal Aging

Surfactant and surfactant/sea water solutions were agedin sealed aging tubes at 100^{o}C for 10 days. Aged surfactant/sea water solutions were vacuum dried. These dried samples were later used for FTIR, NMR and TGA analyses.

4.2.4 Rheological and Thermal Characterization

Discovery hybrid rheometer (DHR-3) from TA Instrument was used for rheological characterization. All rheological measurements were conducted using concentric cylinder geometry having cup diameter of 30.39 mm and bob diameter of 27.99 mm. A shear rate ranging from 0.01to1000s^{-1} and a frequency from 0.1 to 100 rad/s were applied for steady and dynamic shear measurements, respectively. All frequency sweep experiments are in the linear viscoelastic region. Unless, otherwise specified, frequency was kept at 1 rad /s in temperature ramps. Thermo gravimetric analysis (TGA) was carried out using SDT Q600 (TA instruments) under nitrogen atmosphere at a heating rate of 10^{o}C/min from 25 to 500^{o}C.FTIR analysis of surfactant samples was conducted in Nicolet 6700 spectrometer. NMR sample was prepared by transferring around 100 mg of surfactant to 5 mm NMR tubes. 600 µl of D_2O was added to the NMR tube. NMR spectra were acquired on a JEOL 500 MHz spectrometer equipped with multinuclear probe.^{13}C NMR, ^{1}HNMR and^{19}FNMR spectra were recorded by collecting 2000, 32 and 4 scans, respectively.

4.3 Results and Discussion

4.3.1 Thermal Stability of the Surfactant

Thermal degradation of the surfactant before and after interactions with salt was studied by TGA, while 1H-NMR, 13C-NMR, 19F-NMR and FTIR were used to evaluate potential structural changes after aging. TGA analysis was performed on dried samples of surfactant and surfactant/sea water solutions under nitrogen atmosphere. Figure 4-1 shows TGA and DTGA curves of surfactant samples before and after interaction with salts. TGA results show that no major thermal events start before100^{o}C. At 150^{o}C and 230^{o}C, 1% and 10% of surfactant weight has been lost respectively. At 321^{o}C half of the material was lost. Complete decomposition was observed above 400^{o}C. As formation water and flooding water contain high quantity of salts, TGA of the surfactant after interactions with sea water was also carried out. It is clear from Figure 4-1 that the thermal behavior of the surfactant is unchanged after interactions with salt. These results suggest that the fluorocarbon surfactant has good short term thermal stability at high temperatures. NMR and FTIR techniques were used to evaluate long term thermal stability of the surfactant. Surfactant solution in the presence and absence of salts was heated at 100^{o}C in sealed aging tubes for a maximum of 10 days. NMR and FTIR analyses were conducted before and after aging at different days. Only aged spectra of maximum aging (10 days) are shown for FTIR and NMR analyses. Any significant structural changes due to thermal degradation and after interaction with salts were identified by NMR. All three possible types of NMR analyses were utilized to find out possible structural changes in the surfactant. 19F-NMR, 13C-NMR and 1H-NMR spectra are shown in figure 4-2 to figure 4-4.19F-NMR of all four samples has similar peaks before and after aging. Similarly, aged and non-aged samples spectra obtained from 1H-NMR and13C-NMR showed no significant structural change. Therefore, NMR techniques

suggest the stability of the fluorocarbon surfactant at 100oC.FTIR spectra of aged and non-aged samples both in the presence and absence of salts are shown in Figure 4-5. The very broad peak around 3600 cm-1 is due to O–H stretching and it is present in all spectra. A strong peak between 2800 and 2900 cm^{-1} is due to C–H stretching. Other peaks in the range of 1000-1500 cm^{-1} are due to C–F, C–H bending and C–O. Like NMR, no significant difference was observed in aged and non-aged surfactant spectra in the presence and absence of salts. From TGA, FTIR and NMR results it is evident that at 100^{o}C the surfactant does not undergo any type of structural changes even

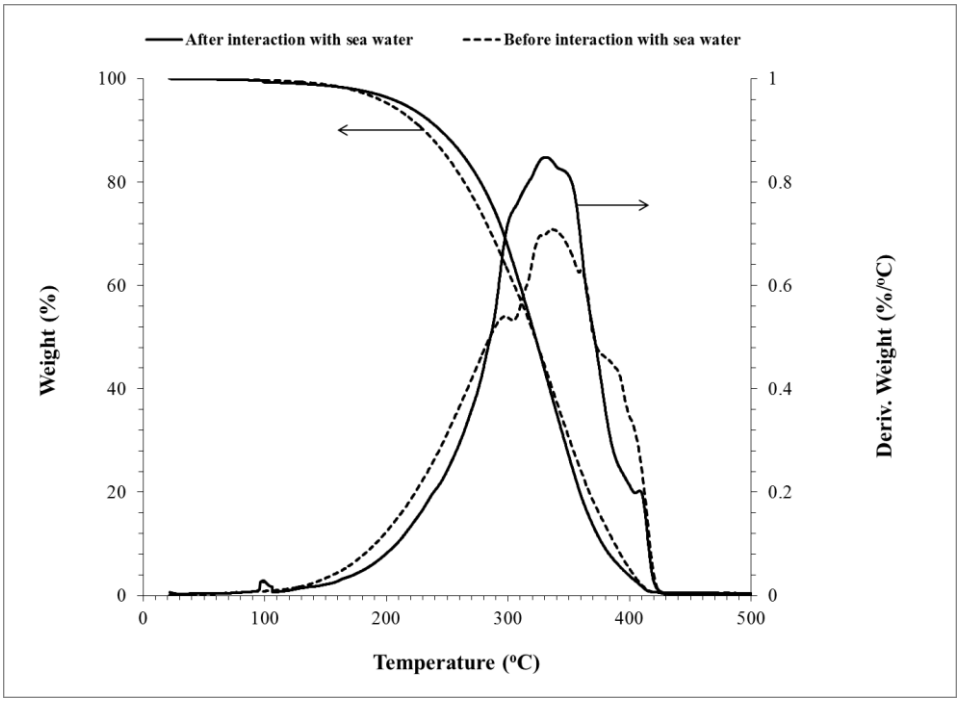

Figure 4-1: TGA and DTGA curves of surfactant under nitrogen atmosphere in the presence of salts.

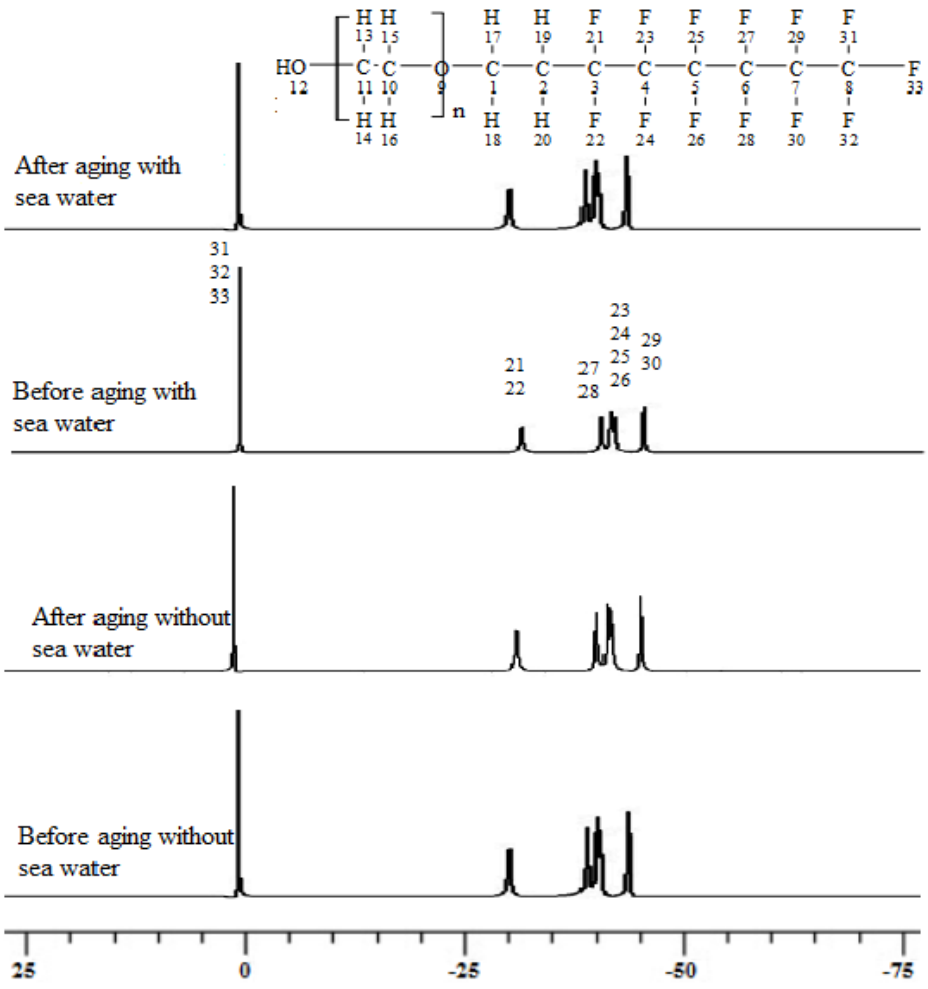

Figure 4-2: ^{19}F-NMR spectra of different surfactant samples

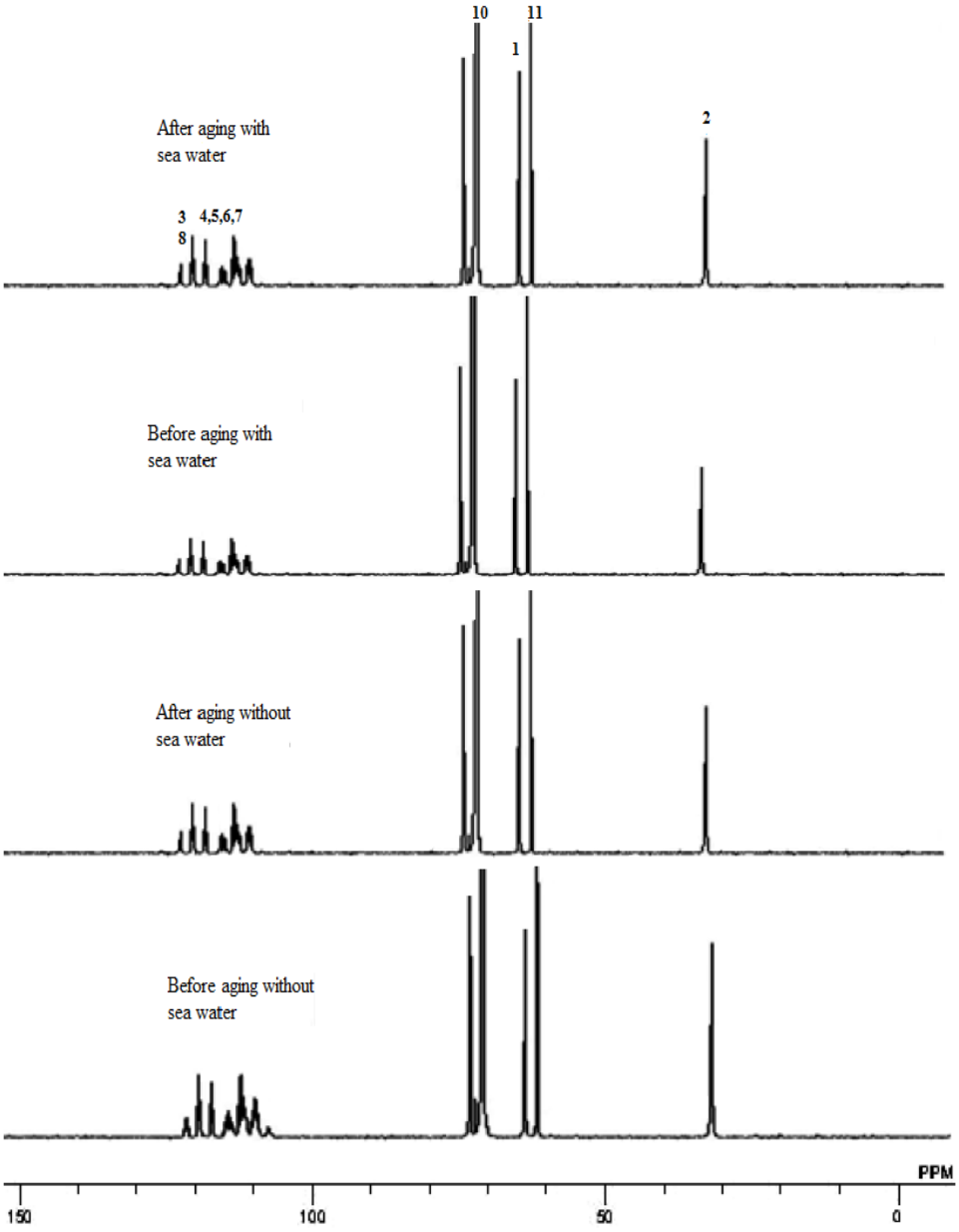

Figure 4-3: ^{13}C-NMR spectra of different surfactant samples

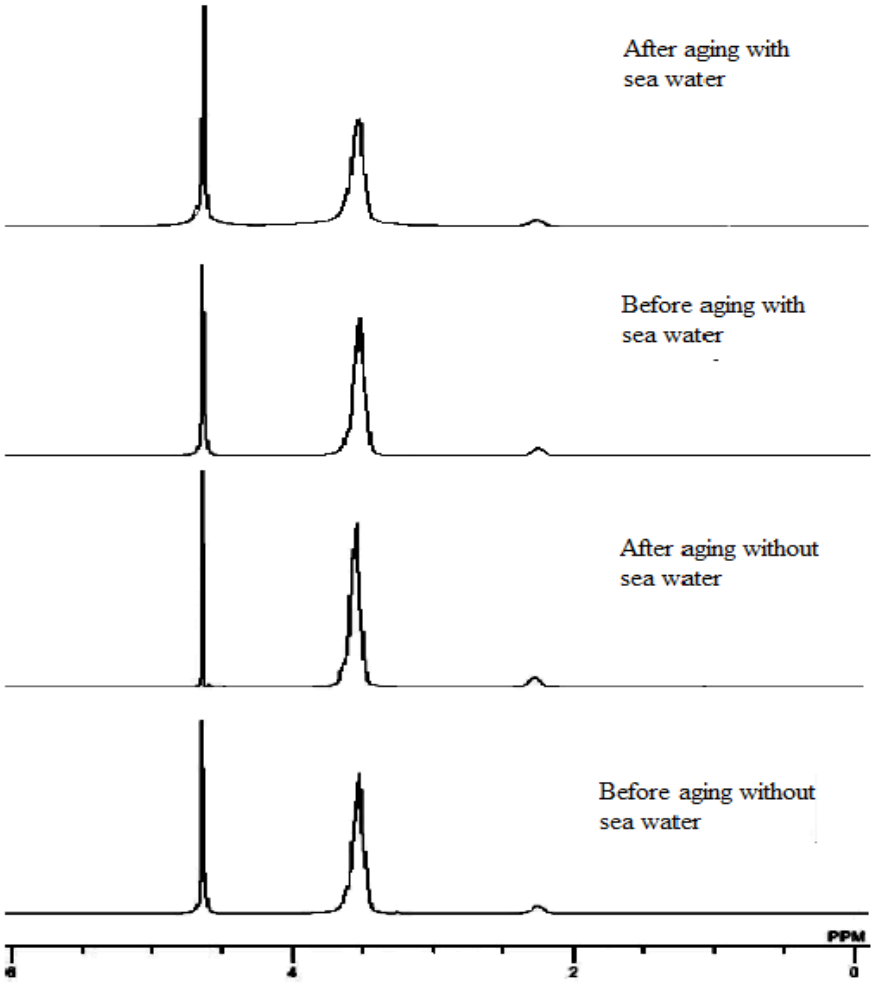

Figure 4-4: ^{1}H-NMR spectra of different surfactant samples

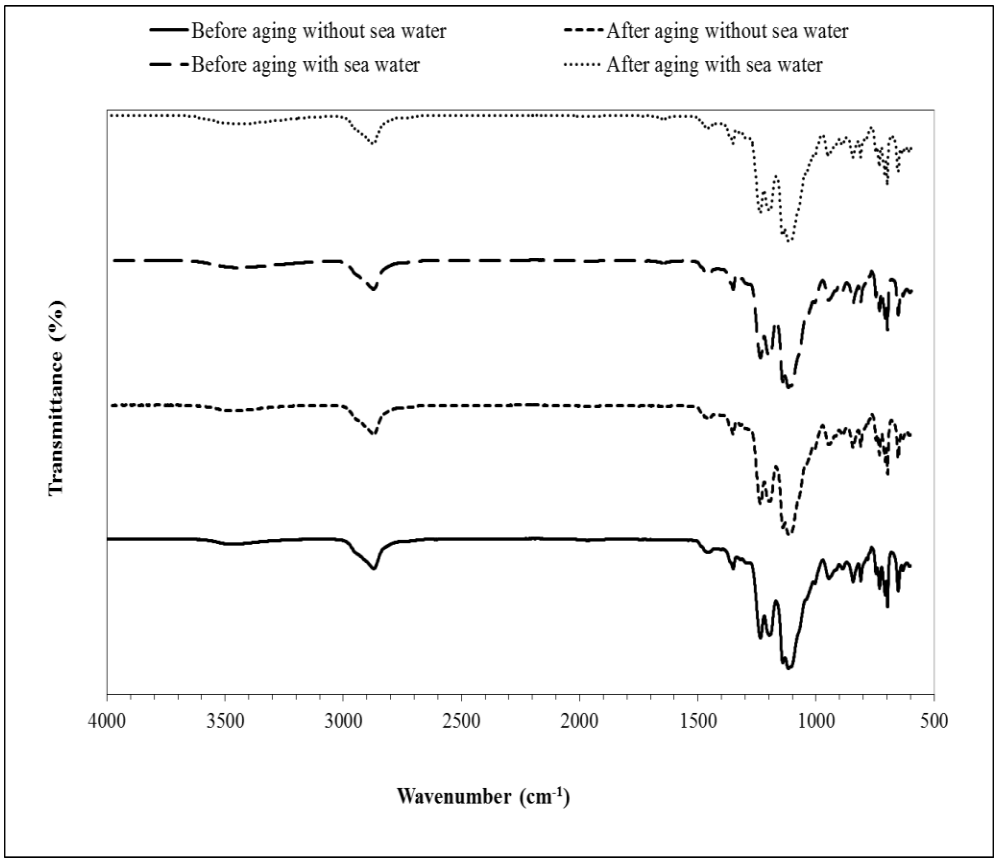

Figure 4-5: FTIR spectra of different surfactant samples

4.3.2 Rheological Behavior of Surfactant-Polymer Solution

Figure 4-6 shows the effect of varying non-ionic fluorocarbon surfactant concentration on steady shear viscosity profile of the copolymer solution in deionized water (DW). Steady shear viscosity at a shear rate of $0.01s^{-1}$ versus surfactant concentration is shown in Figure 4-7. The investigated range of surfactant concentration is between 0.025 to 0.2 %. Addition of non-ionic surfactant has different influence on the rheology of the polymer solution depending on the amount of added surfactant. Ethoxylated non-ionic surfactants develop a variety of microstructure in the presence of water soluble–polymers(Robert, Laurer et al. 2002).Initially, the polymer solution viscosity increases with the addition of surfactant. Further increase in surfactant concentration results in

lowering the viscosity. This type of behavior has also been reported by other authors for non-ionic surfactant–polymer systems (Kientz and Holl 1994; Wang, Tiu et al. 1996; Robert, Laurer et al. 2002). Initial increase in the viscosity is due to hydrogen bonding between surfactant and polymer molecules. Addition of more surfactant results in viscosity reduction due to surfactant-polymer interactions. These interactions occur because excess surfactant molecules surround the polymer molecules and reduce the strength among ions present on the polymer chain. Hence, charge repulsion and molecular expansion factor decrease and results in a decrease in the viscosity. Similar trend has also been reported for non-ionic surfactant-associating polymer systems(Zhao, Khin et al. 2005; Kim, Kim et al. 2007). In this type of system, at sufficiently low surfactant concentration, initial increase in the viscosity is due to formation of mixed micelle and increased hydrophobic association. All the surfactant molecules associate with polymer and there exist no free micelles. But, further addition of surfactant will result in the formation of free micelles as no site is available for surfactant–polymer association at high concentration. As a result, the viscosity decreases due to disruption of intermolecular association. Zero shear viscosity (η_o) and consistency index (k) of Cross Model for different surfactant concentrations are given in Table 4-1. The increase in the viscosity with the addition of surfactant is not significant at high shear rate and infinite shear rate viscosity is almost independent of surfactant concentration. But at low shear rate the effect of surfactant is noteworthy (Figure 4-7 and η_o data provided in Table 4-1). High shear rate breakdown SP complex and therefore the effect of the surfactant is not prominent at high shear rate. Constant *n* (power law index+1) was found to be 0.72 for all surfactant concentrations while η_o increase with the addition of the surfactant. It shows that shear thinning is independent of surfactant concentration. Dynamic rheological tests were also used to study rheological properties of SP solution. Many dynamic rheological

properties are important as they affect efficiency of oil recovery. Storage modulus is a direct indication of the elasticity of materials. It has been proven that an increase inelasticity, increases oil recovery by increasing microscopic efficiency (Wang, Cheng et al. 2001; Wang, Xia et al. 2001; Xia, Ju et al. 2004; Xia, Wang et al. 2004; Xia, Wang et al. 2007; Kuru 2010; Zhang, Li et al. 2011).Increasing surfactant concentration also causes light increase in storage modulus as shown in Figure 4-8. Addition of surfactant is improving the rheological properties in two ways. Increase in viscosity will improve the macroscopic efficiency while increase inelasticity will help increasing the microscopic efficiency.

Change in the rheological properties due to surfactant addition was also investigated at higher temperatures. Flow curves of polymer solution with and without surfactant at two different temperatures are shown in Figure 4-9. At 50^{o}C, the viscosity at low shear rate is high for a polymer solution with 0.025% surfactant compared to the solution without surfactant. But at high temperature (90^{o}C) and low shear rate, viscosity slightly decreases by adding the surfactant in the polymer solution. Results of temperature ramp experiments at ramp rate of 2^{o}C/min are presented in Figure 4-10 and 4-11.Polymer solution with maximum surfactant concentration (0.05%) has the highest storage modulus and viscosity at low temperatures (40^{o}C). But at high temperature (85^{o}C), storage moduli of polymer and SP solutions are almost similar. Arrhenius fit was used to calculate flow activation energy (Ea) and pre-exponential factors (A) given in Table 4-2. The maximum decrease in the viscosity was obtained for the SP system with the highest surfactant concentration. There is no significant change in the activation energy as the surfactant concentration is increased; however, influence of the surfactant concentration on pre-exponential factor is noteworthy (Table 4-2). There-exponential factor is the lowest for maximum surfactant concentration and vice versa. From the above results it can be concluded that at low temperature,

addition of surfactant increases the viscosity while at high temperature slight decrease in the viscosity was observed. Both temperature ramp and steady shear viscosity data support the above conclusion. However, in all cases this increase or decrease in the viscosity is minimal. Overall, the influence of non-ionic ethoxylated fluorocarbon surfactant on the viscosity of the SP system is weak.

Comparative steady shear results of 0.025% surfactant concentration and varying polymer concentration at 50^{o}C are shown in Figure 4-12. Polymer concentration was varied from 0.10 to 0.40%. Figure 4-13 is obtained at constant shear rate of 1s^{-1}.The slope of viscosity concentration curve increase at 0.25% concentration. At a given shear rate, the steady shear viscosity increases with the increase in polymer concentration. The storage modulus at all temperatures increases with the increase in the polymer concentration. Similarly, a decrease in the storage modulus was observed with increase in temperature at all polymer concentrations as shown in Figure 4-14. This reduction in storage modulus with temperature is independent of polymer concentration. For all investigated polymer concentrations, about 30% decrease in the storage modulus was observed as a result of increasing the temperature from 30 to 85^{o}C.The decrease in the viscosity with temperature is also independent of polymer concentration as shown in Figure 4-15. About 25% decrease in viscosity was observed for all polymer concentrations, when temperature was increased from 30 to 85^{o}C with a constant heating rate of 2^{o}C/min. Flow activation energy and pre-exponent factor was also calculated for SP solutions of different polymer concentrations as shown in Table 4-3. Flow activation energy is almost similar for all SP solutions regardless of polymer concentration.

Both field water and sea water contain different types of salts. These salts bring different cations and anions to the solution. These counter-ions may affect the SP solution in many different ways. Their interactions with the surfactant may cause the precipitation of surfactant. They can also interact with polymer and affect it in two ways: precipitation and viscosity reduction. In this study the effect of NaCl, $CaCl_2$, $MgCl_2$ and Na_2SO_4 on the surfactant, polymer and SP system was evaluated. Also, synthetic sea water was prepared in the lab with57,638 ppm total dissolved salts and 2,732 ppm divalent cations. Clear solutions were obtained when surfactant was dissolved in different salt solutions and no precipitation was observed. Also, no precipitation was observed in polymer and SP solutions in different salts. Fixed polymer concentration of 0.25% and surfactant concentration of 0.025% was used to study the effect of salts on the rheological properties. Figure 4-16 shows the influence of NaCl concentration on steady shear viscosity of SP solution. Reduction in viscosity with addition of sodium chloride was observed at all shear rates. Higher viscosity of SP solution in deionized water is due to repulsive forces among the anions present along the polymer chains. The polymer chain remains in the stretched form in deionized water due to repulsion of anions present along the polymer chain. Addition of sodium chloride brings the counter-ions Na+ which neutralize these anions and polymer chain coils up. This charge neutralization and chain coiling reduces the viscosity of SP solution. Similar results were also obtained for sodium sulphate as shown in the Figure 4-17.Dynamic rheological test was also carried out to study the effect of counter-ions on storage modulus. Reduction in storage modulus was observed with addition of sodium sulphate as shown in the Figure 4-18. This reduction is prominent at all frequencies. Rheological behavior of SP solution in sea water was also studied. SP solutions were prepared in sea water of total salinity 57,638 ppm and diluted sea water (25%SW and 75%DW). Flow curves of SP solutions in SW are shown in Figure 4-19.

Drastic decrease in viscosity was observed when SP solution was prepared in SW instead of DW. Dilution of SW with DW results in shifting the flow curve slightly above the flow curve of SW. Viscosity decrease is directly proportional to total salinity. Still with the maximum salinity the viscosity of the SP system is about 10 times higher than the viscosity of water which is reasonable for EOR for specific reservoir conditions (Gao).

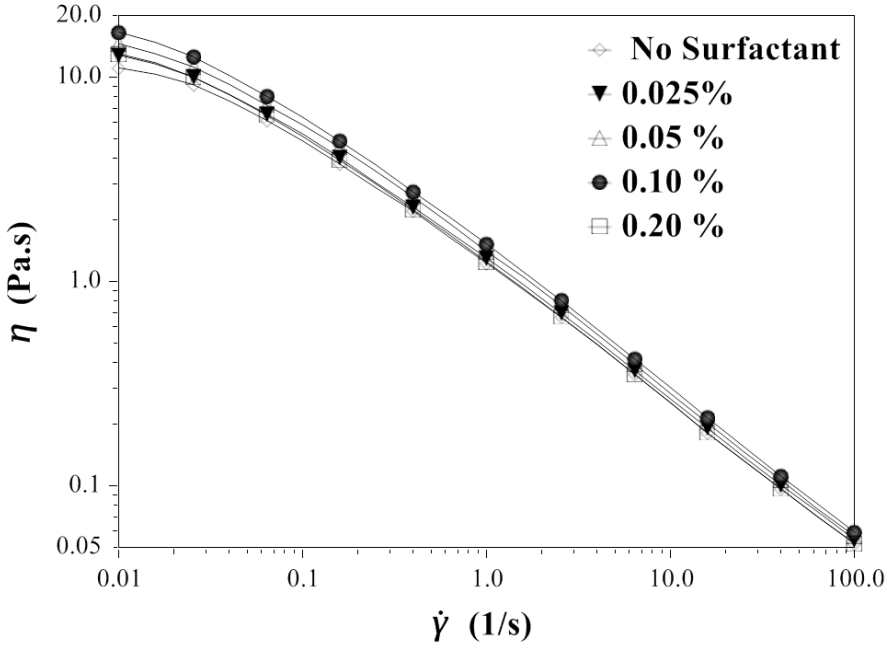

Figure 4-6: Steady shear viscosity profile of SP solutions having different surfactant concentration in salt free water at 50^{o}C

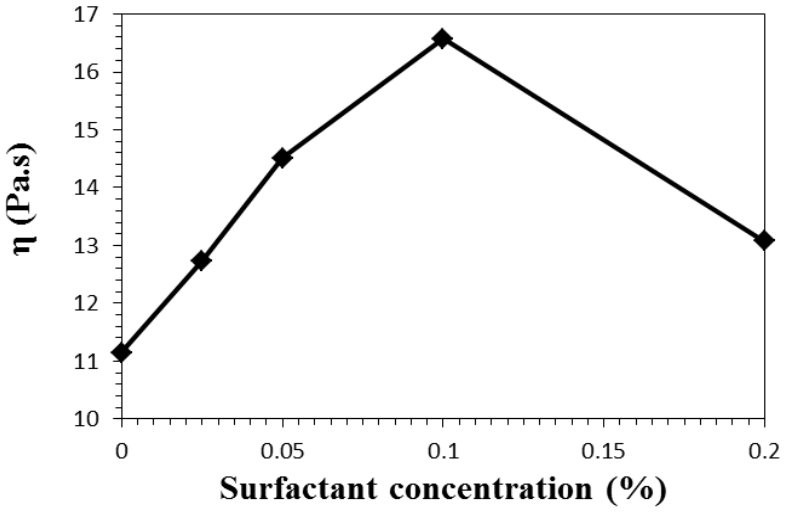

Figure 4-7: Effect of surfactant concentration on steady shear viscosity of polymer at 50^{o}C

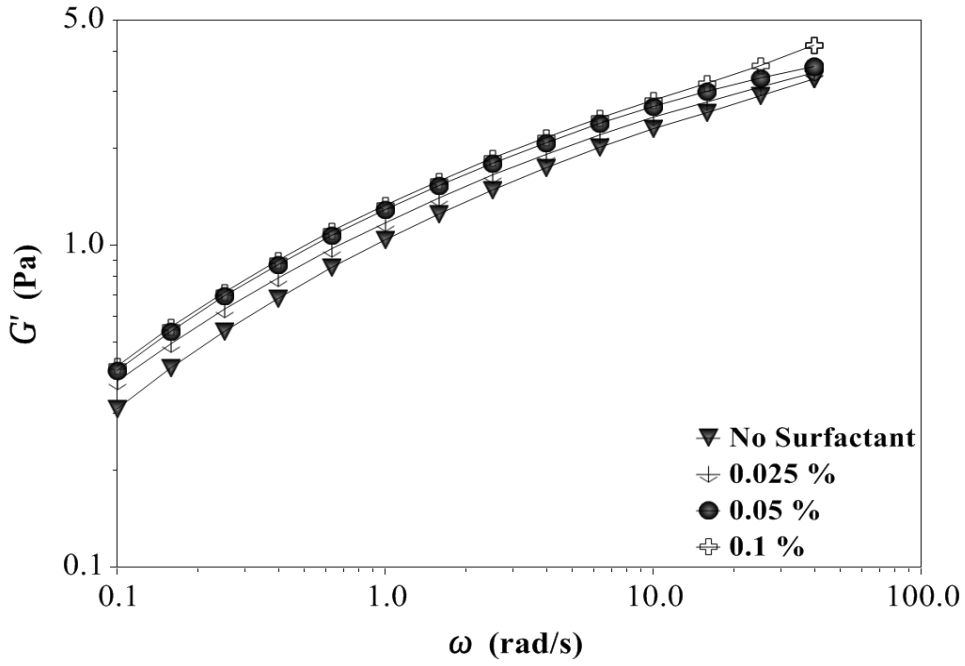

Figure 4-8: Effect of surfactant concentration on storage modulus at 50^{o}C in salt free water

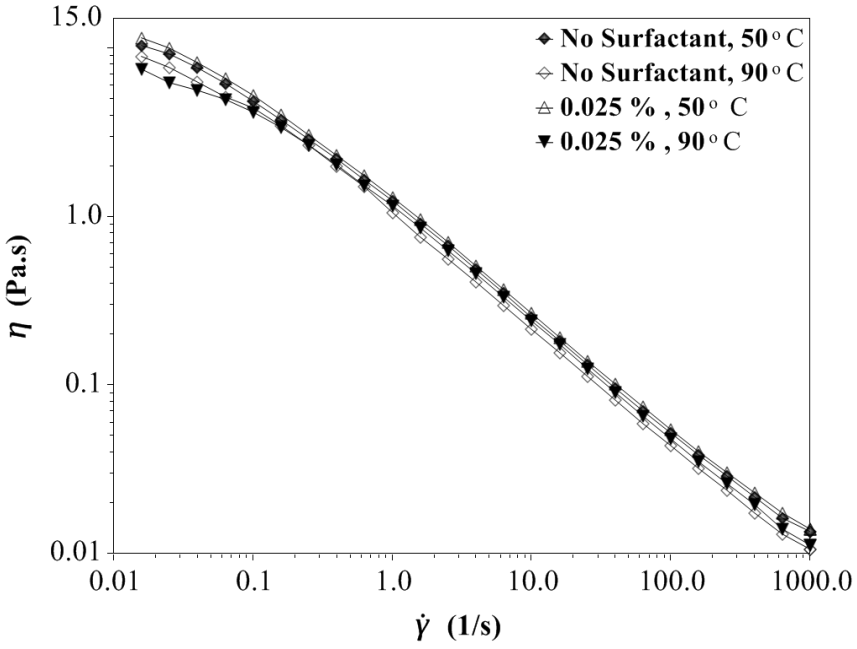

Figure 4-9: Steady shear viscosity profile of 0.25 % polymer solution with and without presence of surfactant at 50 and 90^{o}C

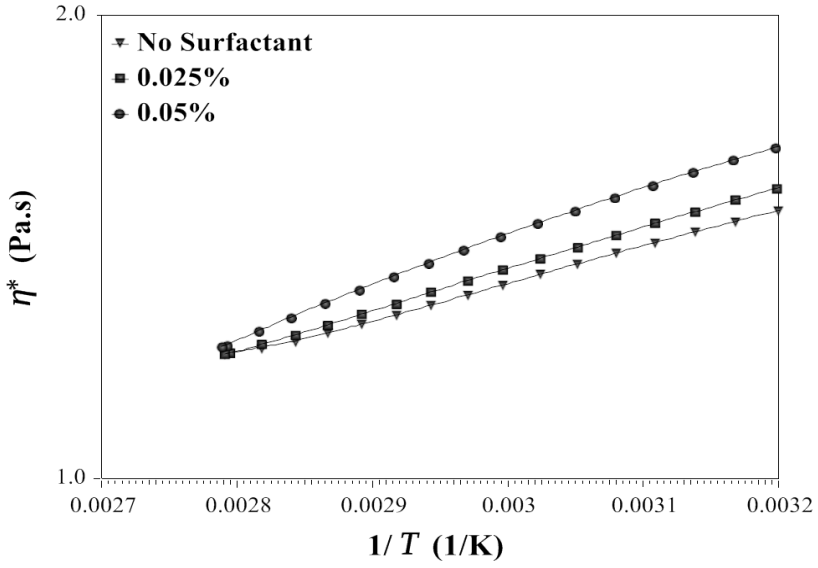

Figure 4-10: Effect of temperature on viscosity of 0.25% polymer solution at different surfactant concentration

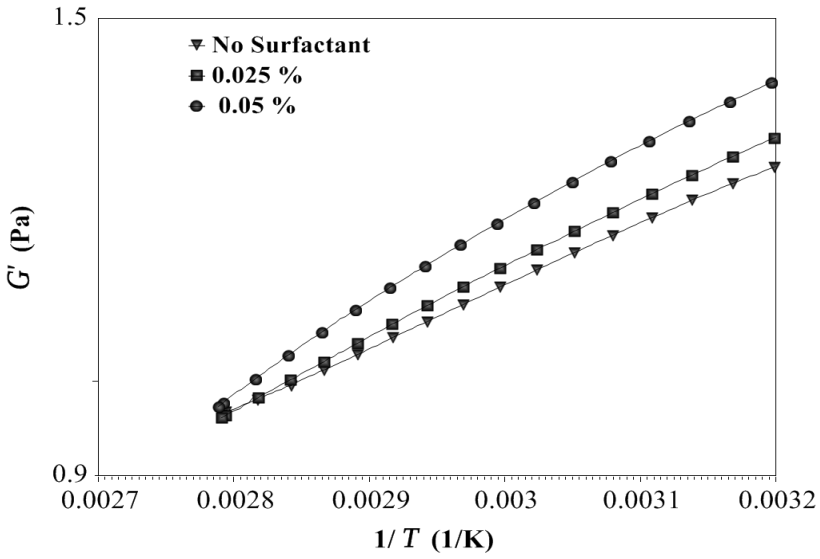

Figure 4-11: Effect of temperature on storage modulus of 0.25% polymer solution at different surfactant concentration

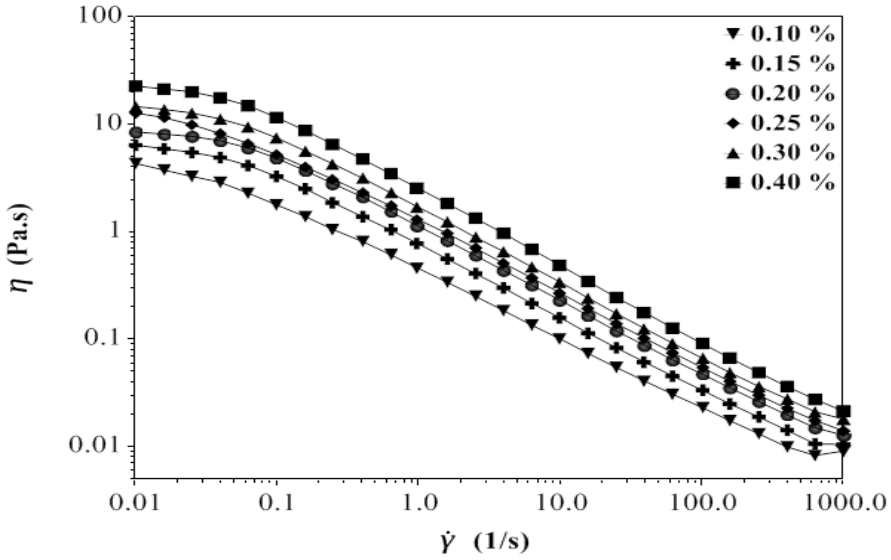

Figure 4-12: Effect of polymer concentration on steady shear viscosity profile of different SP solutions at different shear rate

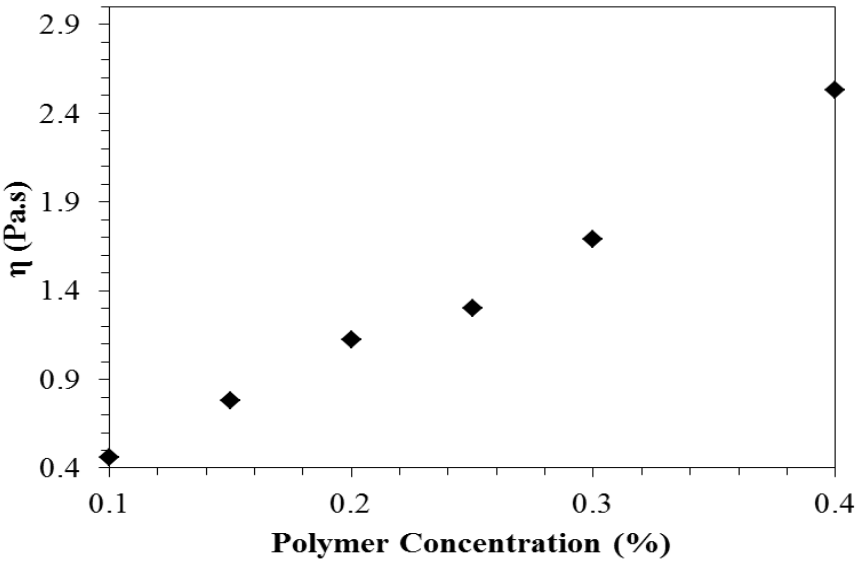

Figure 4-13: Effect of polymer concentration on steady shear viscosity profile at 50^{o}C and shear rate of 1 s^{-1}

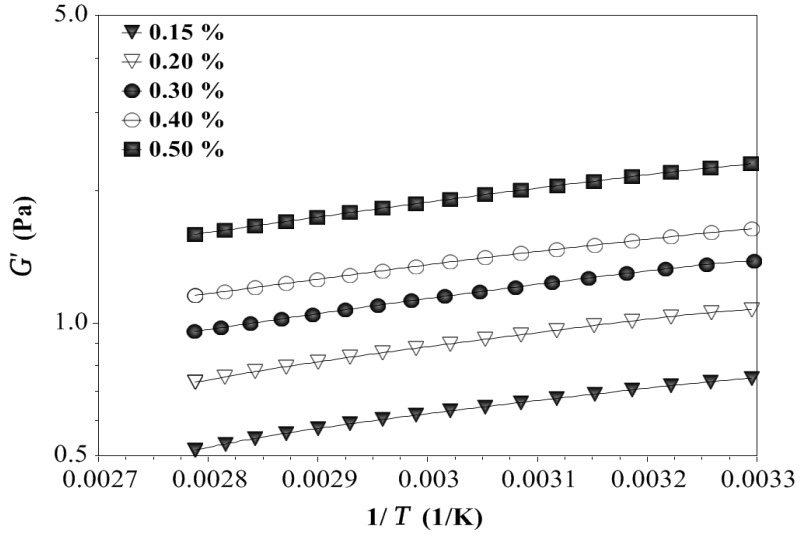

Figure 4-14: Effect of polymer concentration on storage modulus of SP solutions at different temperatures

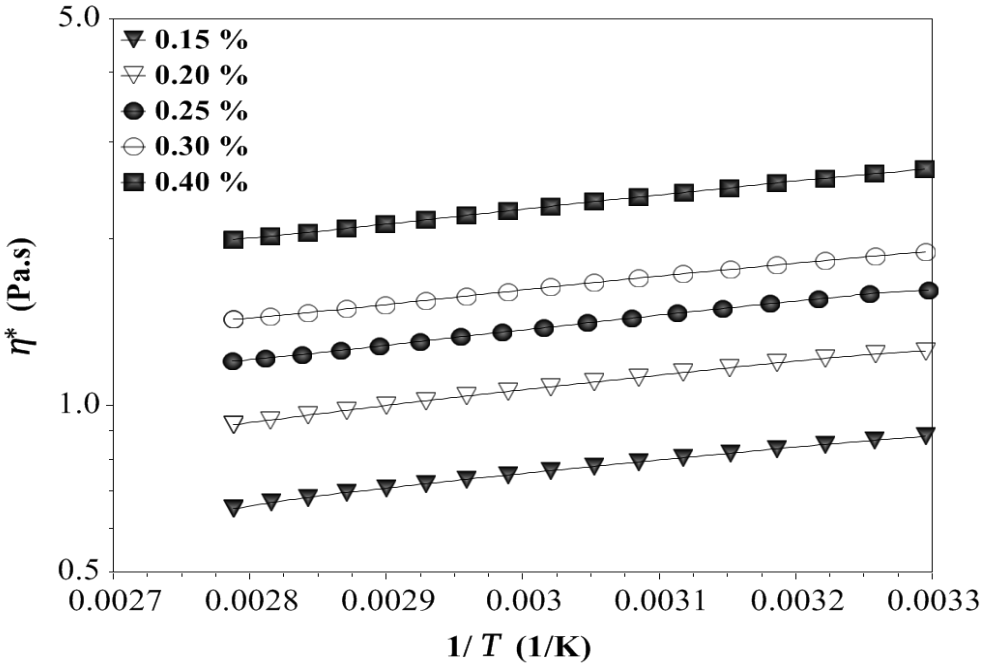

Figure 4-15: Effect of polymer concentration on viscosity of SP solutions at different temperatures

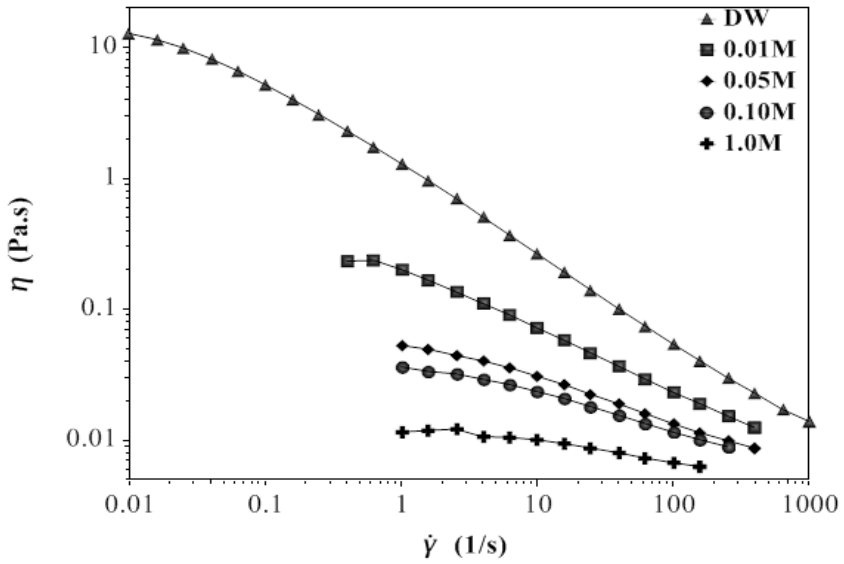

Figure 4-16: Effect of NaCl concentration on steady shear viscosity

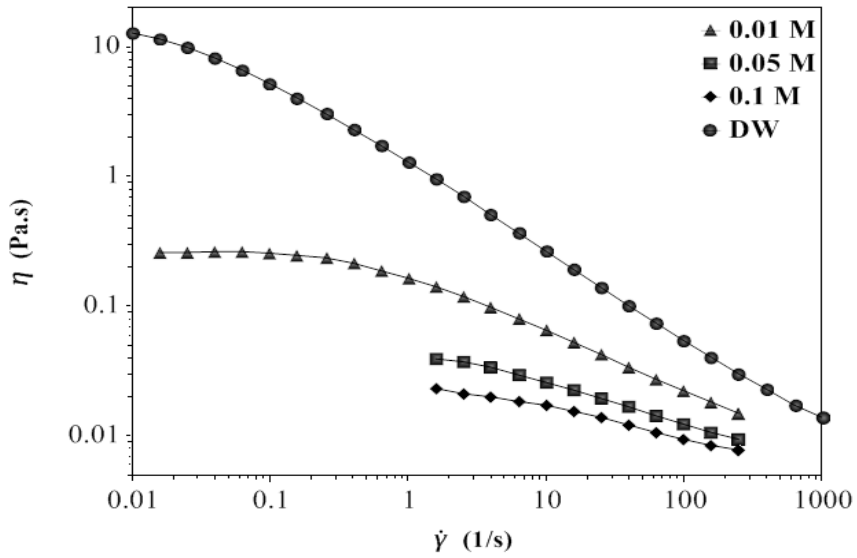

Figure 4-17: Effect of Na_2SO_4 concentration on steady shear viscosity at 50°C

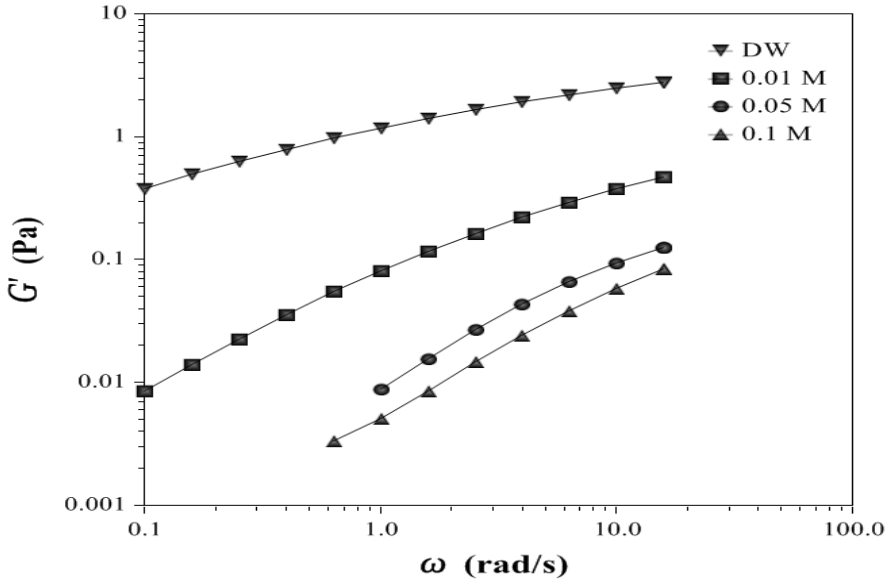

Figure 4-18: Effect of Na_2SO_4 concentration on storage modulus of SP solution at various frquencies

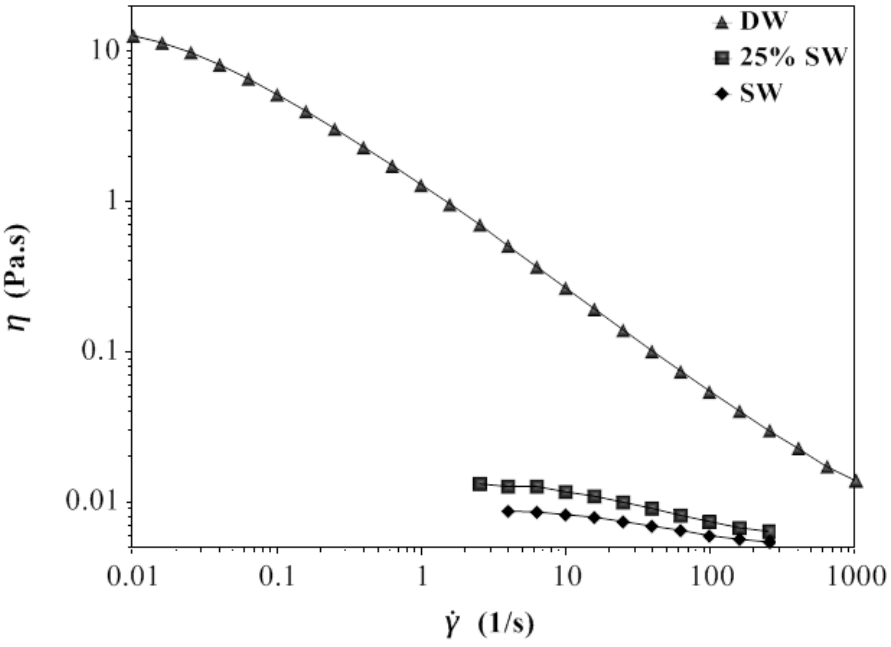

Figure 4-19: Effect of sea water dilution on steady shear viscosity

Table 4-1: Rheological parameters of Cross Model

Concentration (wt %)	η_o (Pa.s)	k (s)
0.000	17.929	39.318
0.025	20.498	44.430
0.050	22.240	40.360
0.100	26.860	49.313
0.200	21.217	48.970

Table 4-2: Flow activation energy and pre-exponential factors for SP solutions at different surfactant concentration

Concentration (wt%)	Ea (kJ/mole)	A (mPa.s)	Decrease (%)
0.000	5.020	210.74	20
0.025	5.046	221.29	25
0.050	5.775	177.68	29

Table 4-3: Flow activation energy and pre-exponential factors for SP solutions at different polymer concentration

Concentration (wt %)	Ea (kJ/mole)	A (mPa.s)
0.15	4.830	130.848
0.20	5.137	166.500
0.25	5.775	177.680
0.30	4.730	292.188
0.40	4.921	382.603

4.4 Conclusions

The investigated fluorocarbon non-ionic surfactant was found to be thermally stable at 100^{o}C. ^{1}H NMR, ^{13}C NMR, ^{19F} NMR and FTIR spectra before and after aging at 100^{o}C are similar and there is no indication of any structural change. The spectra obtained by surfactant aging in the presence of sea water are also similar to non-aged surfactant spectra that indicate surfactant stability in the presence of salts at high temperature. From TGA and DTGA curves, it was concluded that thermal decomposition of surfactant solution after interaction with sea water is similar to original surfactant solution. No weight loss was observed up to 100^{o}C for both surfactant solutions. Upon addition of a non-ionic fluorinated surfactant, slight change in rheological properties was observed. This change in rheological properties depends on temperature and concentration of added surfactant. At low temperature, initially viscosity increases with the increase in surfactant concentration. However, further addition of surfactant reduces the viscosity due to decrease in charge repulsion. At high temperature, viscosity increase was not observed even at low surfactant concentration. Overall, the influence of non-ionic ethoxylated fluorocarbon surfactant on the viscosity of SP system was weak particularly at high temperature and high shear rate. Sea water causes a major drop in the viscosity of SP solutions but still this viscosity is manifold higher compared to viscosity of water.

4.5 Acknowledgements

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CHAPTER 5

RHEOLOGICAL PROPERTIES OF THERMOVISCOSIFYING POLYMER IN HIGH-TEMPERATURE AND HIGH-SALINITY ENVIRONMENT

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Abstract

Thermo-viscosifying polymers (TVPs) are novel class of materials developed for enhanced oil recovery (EOR) applications in high-temperature and high-salinity (HTHS) oil reservoirs. The rheological properties of the TVP-fluorocarbon surfactant and their interactions with different salts were studied. The effects of surfactant concentration, polymer concentration, salinity and different inorganic salts on the rheological properties of the TVP and the surfactant-polymer (SP) system were evaluated. Critical association temperature (T_{cass}) was found to be a function of the TVP concentration and salinity. At low salinity, only thermo-thinning behavior was observed in the entire temperature range. At high salinity, thermo-thinning was obtained in the low temperature range ($<T_{cass}$) followed by thermo-thickening at high temperatures ($>T_{cass}$).The interfacial tension between the crude oil and the TVP solution was reduced by 3 orders of magnitude by using a combination of a fluorocarbon surfactant and a co-surfactant. About 22% additional oil recovery was obtained using the TVP and the SP injection. The TVP showed much better performance and promising results at HTHS conditions compared with commercially available partially hydrolyzed polyacrylamide (HPAM). At HTHS conditions, HPAM suffers huge viscosity loss due to thermo-thinning and charge screening. On the other hand, the high viscosity of the TVP due to thermo-thickening increases the oil recovery at HTHS conditions. The thermo-thickening tendency is enhanced by high temperature and high salinity which makes it more promising for EOR.

Keywords: Rheology; thermoviscosifying polymers; salinity; enhanced oil recovery; polymer flooding

5.1 Introduction

Chemical enhanced oil recovery (cEOR) is a technique to recover residual oil from light oil reservoirs by using surfactant (S), polymer (P) and/or alkali. Some surfactants like alcohol propoxylate sulphate are used to generate ultra-low interfacial tension (IFT) between crude oil and water. This ultra-low value is necessary to increase the capillary number and to overcome capillary forces. Alkalis were usually used to decrease adsorption and for in-situ generation of surfactant by reaction with certain components present in the crude oil(Wang, Zhao et al. 2010). Polymers are normally used to increase the viscosity of displacing fluid so as to improve mobility ratio and increase macroscopic and microscopic displacement efficiency (Wang, Cheng et al. 2001; Wang, Xia et al. 2001; Xia, Ju et al. 2004; Xia, Wang et al. 2004; Xia, Wang et al. 2007; Kuru 2010; Zhang, Li et al. 2011).

Partially hydrolyzed Polyacrylamide (HPAM) is one of the most widely used water soluble polymer for cEOR applications. Due to shifting of oil production towards more deeper and high-temperature and high-salinity (HTHS) reservoirs, conventional HPAM cannot be used to viscosity the displacing fluid at HTHS conditions(Doe, Moradi-Araghi et al. 1987; Veerabhadrappa, Urbissinova et al. 2011), where huge viscosity reduction of HPAM occurs due to charge shielding effect(Lee, Kim et al. ; Mandal and Ojha 2008). HPAM also hydrolyzes at high- temperature, and the hydrolyzed products tend to form complexes with the divalent cations (Ca^{+2}, Mg^{+2}) which are normally present in the reservoir brine, leading to demising or precipitation(Zaitoun and Potie). Thermally stable and salt tolerant water soluble polymers are required to recover the major fraction of remaining oil from HTHS reservoirs. Many researchers have tried to improve the performance of HPAM by incorporating thermally stable monomers or incorporating

hydrophobic side chains (Feng, Billon et al. 2002; Ma, Cui et al. 2002; Ma, Huang et al. 2005; Rico-Valverde and Jiménez-Regalado 2009; Zhang, Wang et al. 2011; Wu, Liu et al. 2012).

Recently, thermo-viscosifying polymers (TVPs) were developed for cEOR applications in HTHS reservoirs to overcome the problems associated with HPAM (Hourdet, L'alloret et al. 1994; Maroy, Hourdet et al. 1998; Petit, Karakasyan et al. 2007; Chen, Wang et al. 2013). In TVP, a thermo-sensitive "block" or "graft" that has the characteristic of lower critical solution temperature (LCST) is incorporated onto the main hydrophilic polymer chain. These thermo-sensitive blocks are soluble in water at room temperature. On increasing temperature, water becomes a poor solvent for these thermo-sensitive blocks resulting in the self-aggregation of these LCST side chains. Above a critical temperature, the self-aggregation and formation of physical networks results in the viscosity enhancement. Further increase in temperature enhances the tendency of network formation and viscosity increases with temperature. The resulting viscosity at high temperature due to the thermo-thickening behavior is highly desirable for EOR applications in HTHS reservoirs.

Detailed rheological properties and factor affecting the rheological properties of novel TVP-fluorocarbon surfactant system were investigated. Comparison of the TVP with two other commercially available water soluble polymers was made under similar conditions. The effects of polymer concentration, surfactant concentration, temperature and salinity on the rheological properties of the TVP-surfactant system were investigated. There is no previous report for SP system consisting of TVP and a surfactant. It is the first time to report an SP system that contains a TVP. Relatively high concentration of the TVP was

used due to its low molecular weight which may increase the cost of EOR. Research is underway to further increase the molecular weight of the TVP.

5.2 Experimental

5.2.1 Materials

Acrylamido tertiary butyl sulfonate/acrylamide (ATBS-AM) copolymer and HPAM were obtained from SNF FLOERGER, France. Molecular weights of these polymers were: 8 and 10 million Dalton, respectively. TVP manufactured in the laboratory of Hengju Polymer Co. (Beijing, China) has a molecular weight of 7.08 million Dalton, 3% degree of hydrolysis degree and8% thermo-sensitive monomer content. All these information are manufacturer provided. The structure of the TVP is shown in Figure 5-1. Amine oxide based amphoteric fluorocarbon surfactant (FS-51) was supplied by DuPont. Carboxyl betaine based surfactant (SS-885) was provided by Oil Chem Technol., USA. Synthetic sea water (SW) and formation water (FW) were prepared using laboratory grade sodium bicarbonate, sodium sulphate, sodium chloride, calcium chloride and magnesium chloride with a total dissolved solids (TDS) of 57,643 mg/L (ppm) and 213,734 mg/L, respectively. Composition of the synthetic SW and FW is given in Table 1.The oil used has a density of 0.8725 g/cm^3 and a viscosity of 13.1 cP. API gravity and molecular weight of the oil are 30 and 251 g/mol, respectively. The polymer solution was prepared using the method described by our group in a previous publication (Kamal, Hussien et al. ; Kamal, Sultan et al.).

5.2.2 Characterization

Discovery hybrid rheometer (DHR-3) from TA Instrument was used for both steady and dynamic rheological measurements. Cone and plate geometry equipped with vapor trap was used. Oscillation temperature ramp experiments were performed in the range 20^{o}C to 90^{o}C with a constant frequency of 1 Hz and constant heating rate of 2^{o}C/min. A shear rate ranging from 1 to 1000 s^{-1} was applied for steady shear viscosity measurements. All reported data points were within the rheometer torque limits (± 5mN.m-2000mN.m).The critical association temperature (T_{cass}) was calculated from plots of viscosity vs. 1/T. More precisely, two straight lines were drawn: one for thermo-thinning region and the other for the thermo-thickening region. Crossover of these two lines gives T_{cass}. IFT between water and crude oil was measured using a spinning drop densitometer supplied by Kruss. Core flooding test was performed at 90^{o}C using Indiana Limestone core. The length and diameter of the core used were 12 inch and 1.5 inch, respectively. The core was first saturated by the formation water followed by saturation with the oil at 90^{o}C. Sea water was injected after aging the core followed by TVP, SP and brine injection. The TVP and the SP solutions were injected at a rate of 0.5 mL/min.

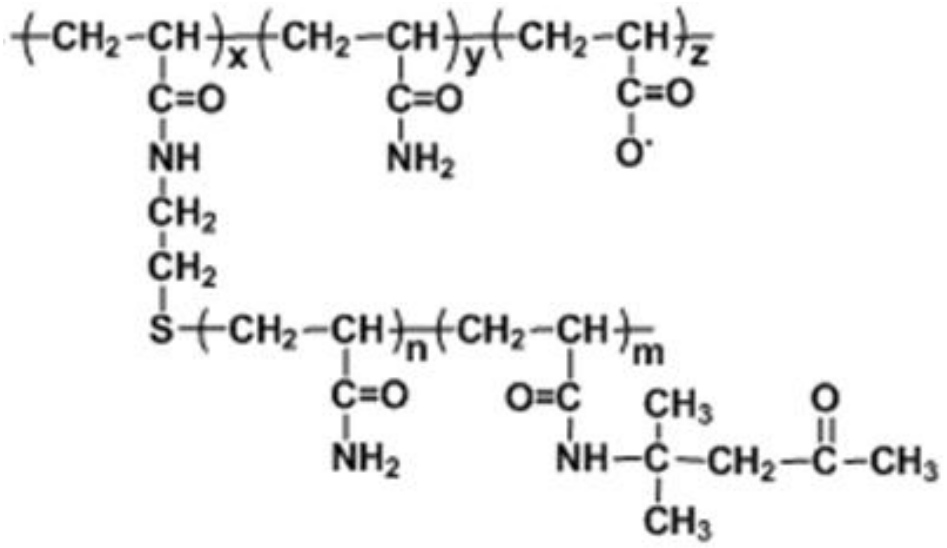

Figure 5-1**:** Molecular structure of the TVP used in the study (x=8wt%, y=89wt%, z=3wt %)

5.3 Results and Discussion

The discussion is divided into four parts. In the first part, rheological properties of the TVP (without surfactant) are discussed. The second part presents the rheological properties of the SP system consisting of the TVP and the fluorocarbon surfactant. In the third part, the interfacial properties of the surfactant and the SP systems are analyzed. Finally, core flooding data and oil recovery obtained by using the TVP-surfactant system is discussed.

5.3.1 Rheological Properties of the TVP

Figure 5-2 shows steady shear viscosity of the TVP solutions in deionized water (DW) and synthetic sea water (SW). The results shown in Figure 5-2 indicate that the rheological behavior is dependent on the concentration of the TVP. At concentrations <0.8%, the TVP solution viscosity was higher in DW in comparison with SW. But at higher polymer concentration (>0.8%), the viscosity of the polymer in SW was higher than that in DW. For SW, viscosity versus concentration(C) data showed the presence of

three different concentration zones. The first zone (dilute solution regime) was for polymer concentrations that were less than 0.4%. For the dilute solution regime, the viscosity was proportional to $C^{1.1}$. The semi dilute regime was from 0.4 to 0.6% in which the viscosity was proportional to $C^{2.1}$. The zone after 0.6% is called concentrated solution regime. The viscosity in this zone was proportional to $C^{3.4}$.The increase in the power index power to 3.4 suggests the formation of physical networks (Hussein, Ali et al. 2010).

Dynamic shear rheological measurements were performed to obtain complex viscosity and elastic modulus. Elasticity of a polymer is another important property for EOR that is related to microscopic sweep efficiency (Zhang, Li et al. 2011). The storage modulus of the TVP in both SW and DW is shown in Figure 5-3. The storage modulus at low TVP concentrations (up to 0.3%) was high in DW compared to SW. But as the concentration of the polymer was increased from 0.4%, storage modulus of the TVP solution in SW was much higher compared to DW. A rapid change can be seen in the storage modulus of the saline solution while for salt-free solution it was almost linear. This increase in the storage modulus at high polymer concentrations in the SW was due to the formation of physical junctions. It shows that inter-chain association was enhanced in the SW. These results support the above findings from steady shear viscosity measurements where the power index has increased to 3.4. Further discussion on the effect of salts is provided in the next section on the SP system.

Another important factor in deciding the inter-chain association is temperature. Therefore, temperature sweep experiments were performed to relate the TVP concentration, temperature and salinity as shown in Figure 5-4. At all concentrations, the viscosity first decreased with temperature, then became constant and finally increased with temperature. At room temperature the thermo-sensitive macro monomer is soluble in

water. The solubility of the thermo-sensitive macro monomer decreased with temperature and the macro monomer starts to self-assemble above T_{cass}. The self-assembly of the macro monomer results in the formation of physical junctions of the reversible network which increased the viscosity of the TVP. However, the T_{cass} at the onset of the thermo-viscosifying effect depends on the TVP concentration and salinity. T_{cass} decreased from 64 to 51^{o}C upon increasing the polymer concentration from 0.3 to 1.0%.

At fixed TVP concentration (0.5%), a comparison of the TVP viscosity behavior, in DW, SW and FW is shown in Figure 5-5. In DW, only thermo-thinning behavior was observed similar to other water soluble polymers. However, in SW, thermo-thinning was followed by thermo-thickening behavior. The most interesting results were obtained for the TVP solution in FW. Total salinity of formation water was much higher (almost 4 times) than SW. The high level of salinity in FW shifted T_{cass} to a lower value and therefore no thermo-thinning region was found in the given temperature range. In summary, T_{cass} was lowered upon increasing the TVP concentration and the thermo viscosifying ability was enhanced by increasing the salinity.

A comparison of the TVP with commercially available HPAM and ATBS-AM copolymer is shown in Figure 5-6. Both HPAM and ATBS-AM copolymer showed thermo-thinning behavior. On the contrary, the TVP showed both thermo-thinning and promising thermo-thickening behavior above T_{cass}. Though the molecular weight of the TVP was lower than HPAM and ATBS-AM copolymer, the viscosity of the TVP was higher in comparison with other polymers at high temperatures (>80^{o}C). This type of behavior is strongly desirable in EOR applications. The low viscosity eases the injection of the polymer solution in the reservoir. In addition, the increase in the viscosity of the injected solution at reservoir conditions of high temperature and high salinity (HTHS) can increase the

recovery efficiency. Due to low molecular weight of the TVP, relatively high concentration was used. Work is underway to synthesize high molecular weight TVP to get high viscosification at low concentrations. The TVP is not a good candidate for low-temperature reservoirs, owing to its low viscosity in comparison with HPAM and ATBS-AM copolymer. However, due to the thermo-thickening behavior above T_{cass}, the TVP is a promising candidate for HTHS reservoirs.

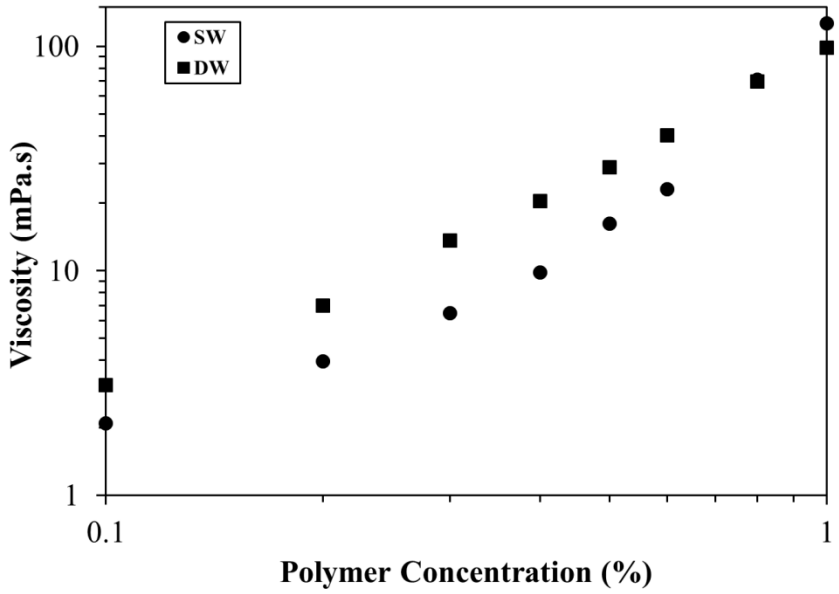

Figure 5-2: Effect of polymer concentration on steady shear viscosity at 70^{o}C and shear rate of 7.3s^{-1}

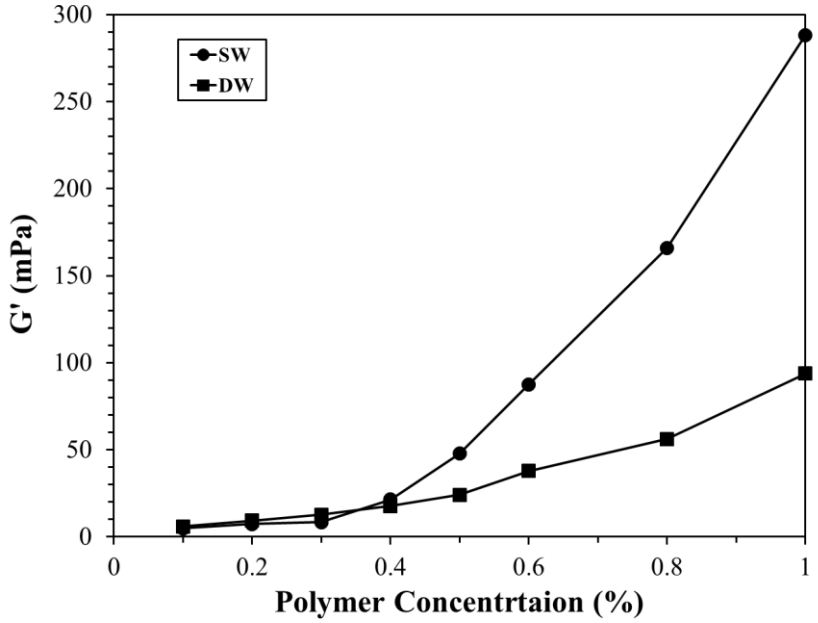

Figure 5-3**:** Effect of TVP concentration on storage modulus at 70 ^{o}C and constant frequency of 1 Hz

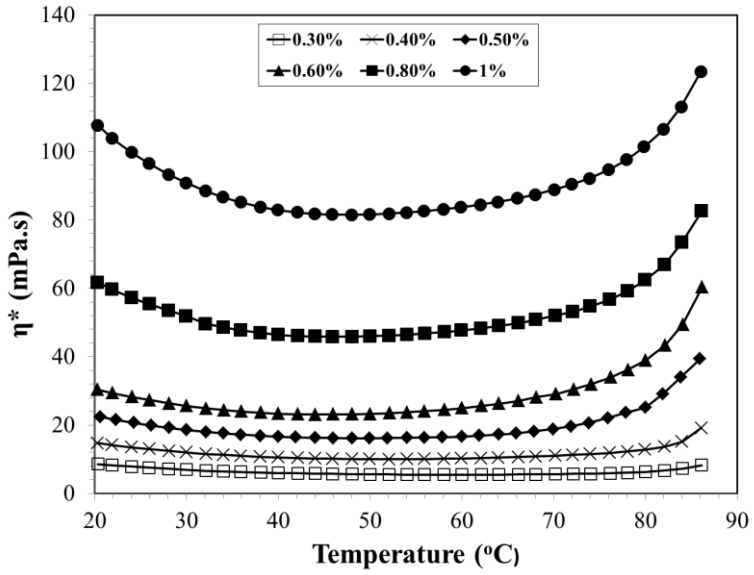

Figure 5-4: Variation of complex viscosity of TVP solutions in synthetic SW at various concentrations

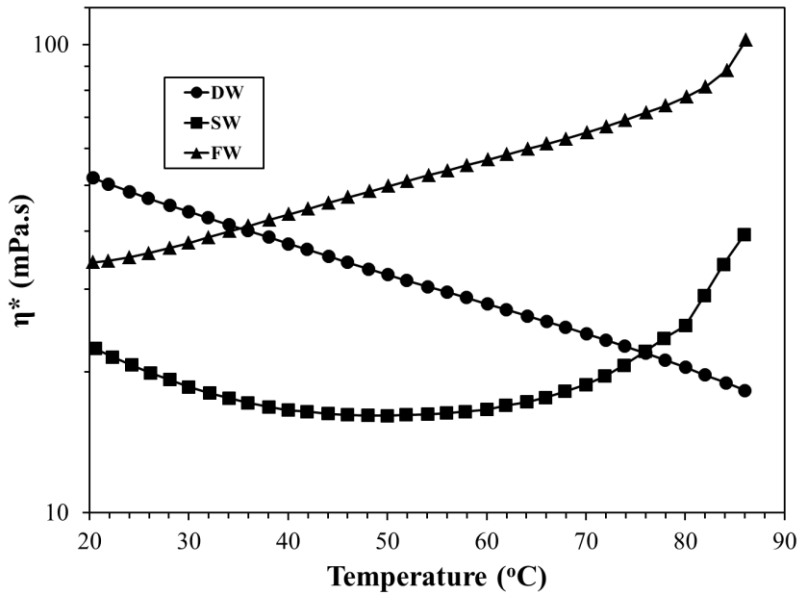

Figure 5-5: Complex viscosity of 0.5% TVP in SW, FW and DW at different temperatures.

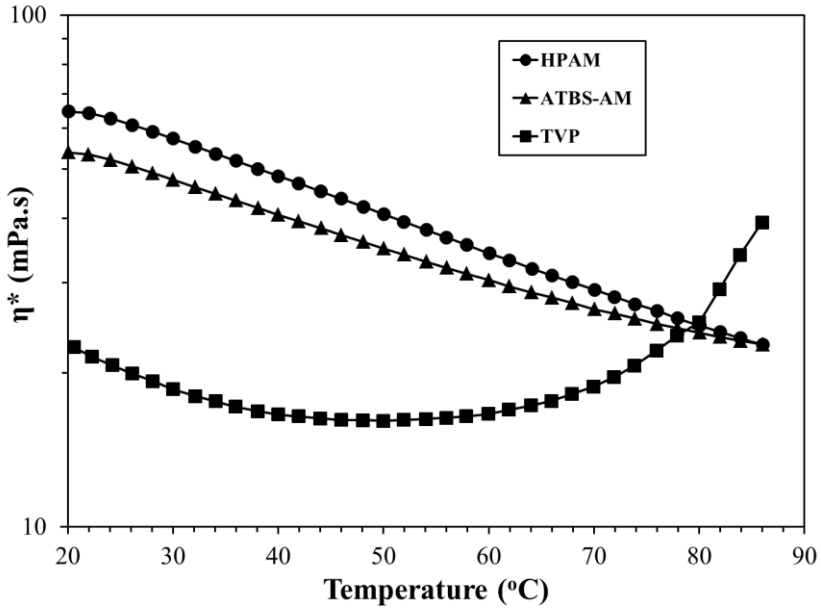

Figure 5-6: Comparison of the viscosity of various water soluble polymers (0.5%) in synthetic SW

5.3.2 Rheological Properties of the SP System

Surfactant-polymer interactions have major impact on rheological properties of SP systems. Therefore, the rheological properties of the SP systems containing fluorocarbon amphoteric surfactant were measured at two different surfactant concentrations. SS-885 was used as a co-surfactant. The fluorocarbon surfactant was selected owing to its good thermal stability under HTHS conditions.

The influence of surfactant concentration on the viscosity of the SP system is shown in Figure 5-7. The complex viscosity increased with the increase in surfactant concentration. This increase was prominent up to T_{cass}. At temperatures higher than T_{cass}, the thermo-thickening behavior of the polymer was dominant. Therefore, at high temperature the impact of surfactant concentration on the complex viscosity of the SP solutions was reduced. Steady shear measurements were also performed on solutions with different surfactant concentrations as shown in Figure 5-8. Steady shear viscosity increased with the increase in the surfactant concentration. The effect of the surfactant concentration was significant at low shear rate only while at high shear rate the effect of shear was more significant.

Based on the data obtained from rheological results of surfactant-free polymer, the salinity and temperature were found to be the two important parameters that affect the performance of the TVP. Salts have a strong influence on aqueous solution properties of the polymer due to their impact on the free energy of interaction between water and the polymer (Liu, Wang et al. 2012).Therefore, the selected SP system was evaluated at fixed TVP concentration (0.5%) and fixed surfactant concentration (0.05%) by varying the salinity of water. At low temperatures up to 70^{o}C, the viscosity of the SP solution in DW

was higher in comparison with SW as shown in Figure 5-9. At high temperatures (>70^{o}C), the solution viscosity in SW was higher. For other water soluble polymers like HPAM and ATBS-AM copolymer, addition of salts decreased the viscosity at all temperatures(Kamal, Hussien et al.). Addition of salts brings counter-ions that weaken the repulsive forces of the negatively charged stretched polymer chain. Polymer chain may collapse due to this charge shielding leading to a reduction in the viscosity. In the case of the TVP, two types of effects can be observed that leads to a change in the viscosity. Firstly, at low salinity, due to the charge screening effect the polymer chain may become flexible and the viscosity may be reduced. Secondly, beyond a certain salinity chain coils up and intermolecular association can happen this may result in increase in the viscosity(Liu, Wang et al. 2012). Also, thermally induced inter-molecular association and formation of physical junctions enhance the viscosity. This association occurs due to aggregation of thermo-sensitive side chains into hydrophobic micro domains to avoid their exposure with water. The decrease in the viscosity with temperature up to 70^{o}C is due to the interactions of counter-ions with the polymer. But above T_{cass}, thermo-thickening effect in the saline solution due to physical junctions was more prominent as compared to charge screening effect. As a result, the viscosity of saline solution increased at high temperatures. Viscosity of the SP solution in FW was higher than the viscosity of the SP solution in DW and SW at all temperatures. In the case of FW, only thermo-thickening region was found. Absence of thermo-thinning region suggests that T_{cass} was already reached and it was much lower than the critical temperature of the SP solution in SW. As FW water has much higher salinity compared to SW (Table 5-1), we can also conclude that the critical temperature decreased to a lower value with the increase in salinity. To further explain the effect of salts on T_{cass},

rheological properties were evaluated at different concentrations of sodium chloride. The concentration of NaCl was varied from 0.1M to 2M and results were compared with polymer solutions in DW. Figure 5-10 shows the complex viscosity of the SP system at different temperatures and different concentration of NaCl. These results were interesting and provide basic understanding of the behavior of the SP system. In DW, the SP system showed thermo-thinning behavior and no thermo-thickening was observed. At 0.1 M NaCl concentration, again thermo-thinning behavior was observed and viscosity at all temperatures was lower than the viscosity in DW. This reduction in the viscosity is due to charge shielding mechanism(Liu, Wang et al. 2012). The viscosity of the SP system in 0.5M NaCl solution was lower than the viscosity in DW at temperatures up to 60^{o}C. Above 60^{o}C, the viscosity of the SP system in 0.5M NaCl solution was higher than the viscosity in DW. At low temperature, charge shielding mechanism dominates while at high temperature the thermo-thickening behavior dominates. With increasing NaCl concentration (1M), the viscosity even at 35^{o}C becomes greater than the viscosity in DW. At 2M NaCl concentration, the viscosity versus temperature curve has no thermo-thinning region. The critical temperature, T_{cass} decreased from 85^{o}C to 53^{o}C upon increasing the concentration of NaCl from 0.1M to 2M. It was concluded that to achieve thermo-viscosifying behavior a minimum salinity is required. With increasing salinity, the critical temperature to attain viscosifying behavior shifts towards a lower value. Steady shear plot for different concentrations of NaCl are shown in the Figure 5-11. These results were consistent with the dynamic rheological results. Effect of NaCl concentration was more significant at low shear rate.

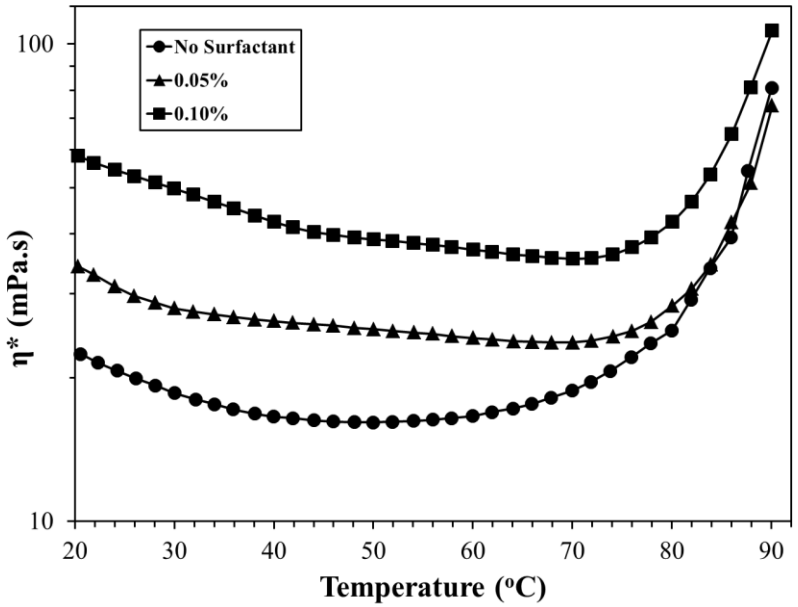

Figure 5-7: Effect of the surfactant concentration on complex viscosity of SP solution at 0.5% TVP concentration

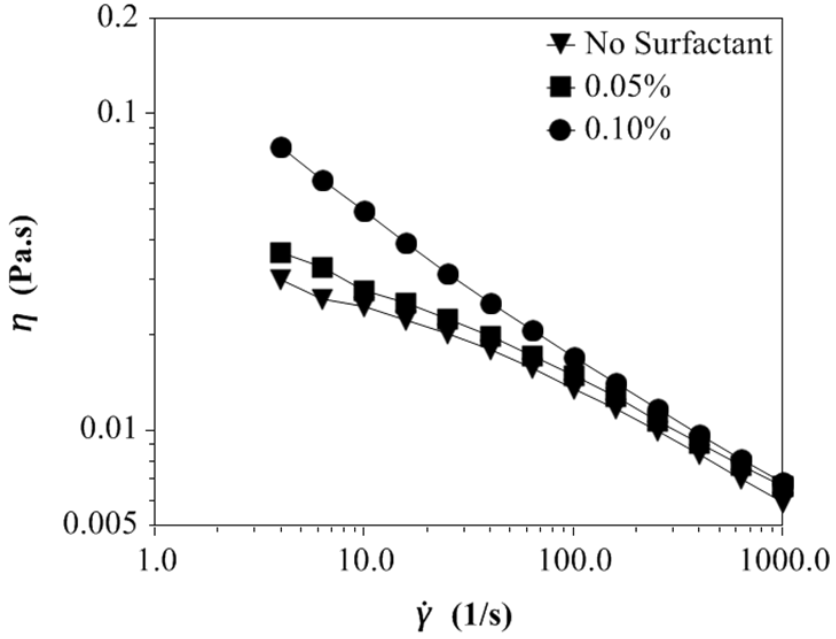

Figure 5-8: Effect of surfactant concentration on steady shear viscosity of 0.5% TVP in the SW at 70°C.

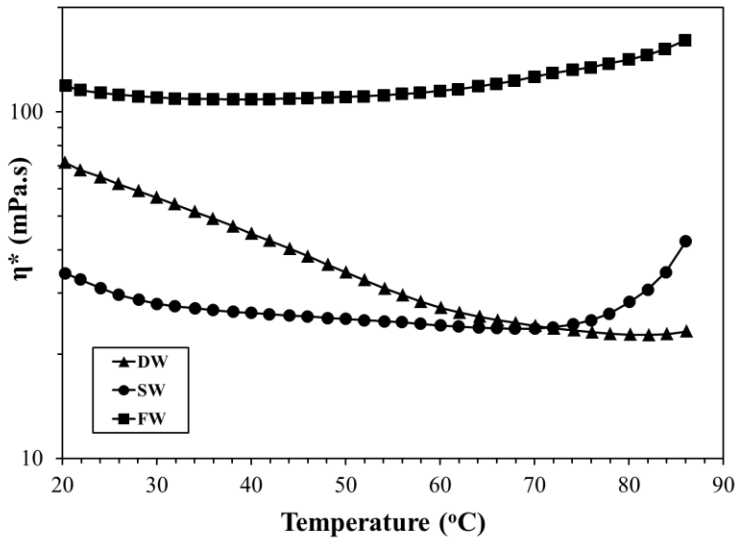

Figure 5-9: Complex viscosity of the SP solutions in SW, FW and DW

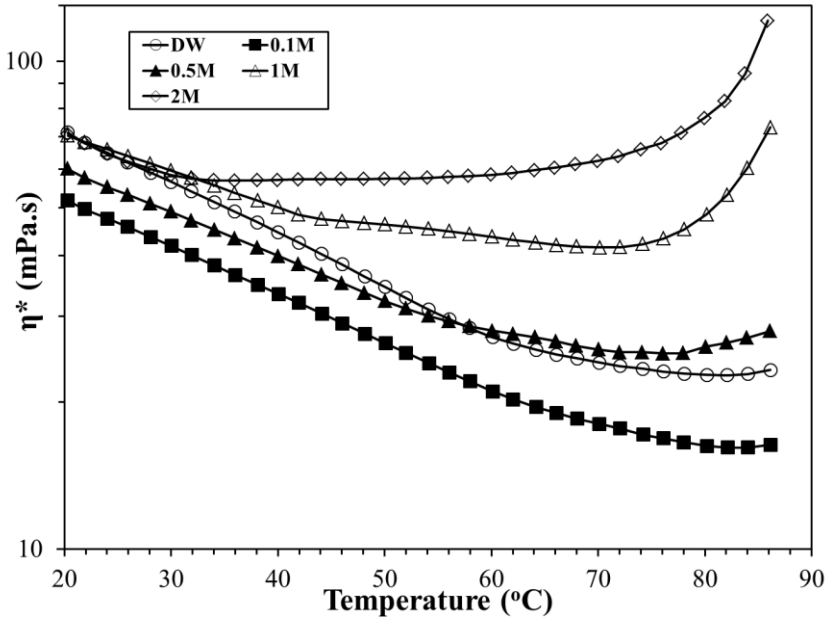

Figure 5-10: Effect of NaCl on the complex viscosity of the SP solution

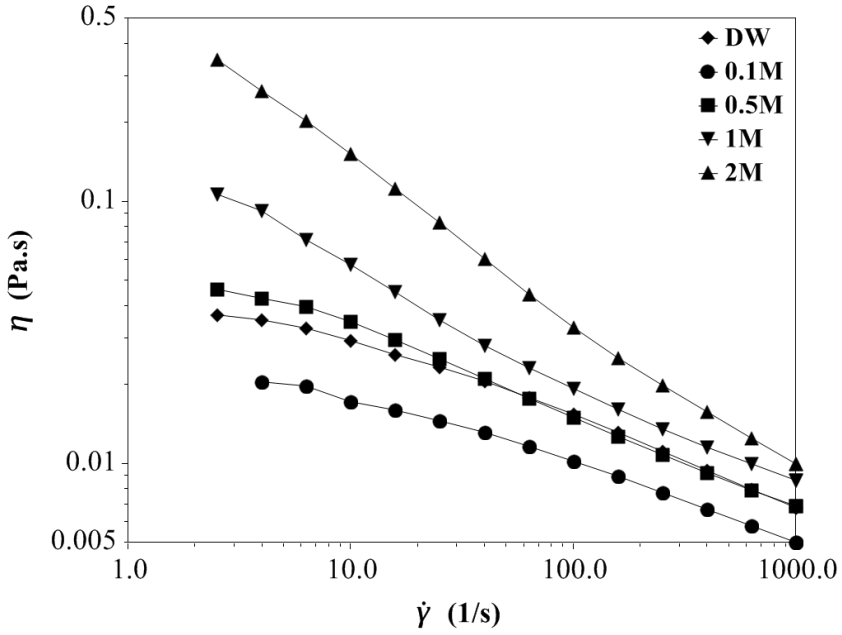

Figure 5-11: Effect of NaCl on steady shear viscosity of the SP solution at 70^{o}C

Table 5-1: Composition of SW and FW

Ions	FW (mg/L)	SW (mg/L)
Sodium	59,491	18,300
Calcium	19,040	650
Magnesium	2,439	2,083
Sulfate	350	4,290
Chloride	132,060	32,200
Bicarbonate	354	120
TDS	213,734	57,643

5.3.3 Interfacial tension Measurements

Interfacial tension for the surfactant and the SP solutions was evaluated at various temperatures as shown in Figure 5-12. Figure 5-12 indicates that addition of the TVP has minute effect on IFT between the crude oil and SW. However, for the surfactant/SW solution, addition of the TVP increased the IFT at high temperatures. This type of behavior was also observed for HPAM/surfactant solution (Wu, Cheng et al.). Enhanced viscosity was obtained due to the addition of the polymer offers higher mass transfer resistance and decreases the mass transfer rate at oil/water interface. However, it is not true always and opposite results have been reported as well (Hongyan, Xulong et al. 2009).For the SW and the TVP/SW solution IFT slightly decreased with the increase in temperature. While for the surfactant and the SP solutions, the IFT slightly increased with the increase in temperature. Addition of 0.05% surfactant reduces the IFT from 10.6 mN/m to 1.7 mN/m. As much lower IFT is required in EOR, different co-surfactant was evaluated to obtain aTVP formulation with a lower IFT. Due to high divalent cations in SW, most of the evaluated surfactants were either incompatible with the brine or thermally unstable. Amphoteric betaine based surfactant SS-885 with good thermal stability and brine compatibility was used as a co-surfactant. Addition of the co-surfactant reduced the IFT to the order of 10^{-2}mN/m.

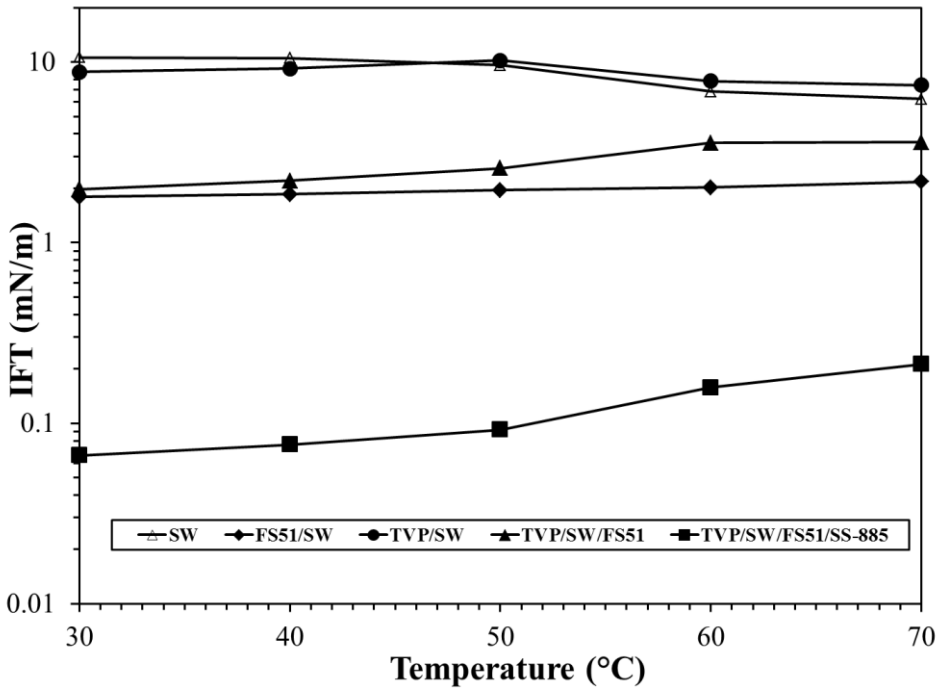

Figure 5-12: IFT of different surfactants and SP systems in SW at 0.5% TVP and 0.05% surfactant concentration

5.3.4 Core Flooding

Typical oil recovery data using the TVP and the SP solution is shown in Figure 5-13. About 40% of the total oil was recovered using SW injection. With the use of the TVP and the SP injection 22% additional oil was recovered. This recovery factor at such severe conditions is encouraging and can be well related to its promising rheological properties. The polymer achieved high viscosity at high-temperatures and high-salinities due to the thermo-viscosifying nature of the polymer. The recovery was obtained using a total of 1.2 PV (Pore Volume) of the TVP and the SP solutions. The molecular weight of the TVP is comparatively low, and synthesis of high molecular weight TVP can reduce the polymer concentration and injected PV to obtain similar recovery. High molecular weight may induce sensitivity to mechanical degradation. But for EOR, commercial polymers have molecular weight as high as 22 million Dalton while the TVP has a

molecular weight of 7 million Dalton which suggests that mechanical degradation is limited.

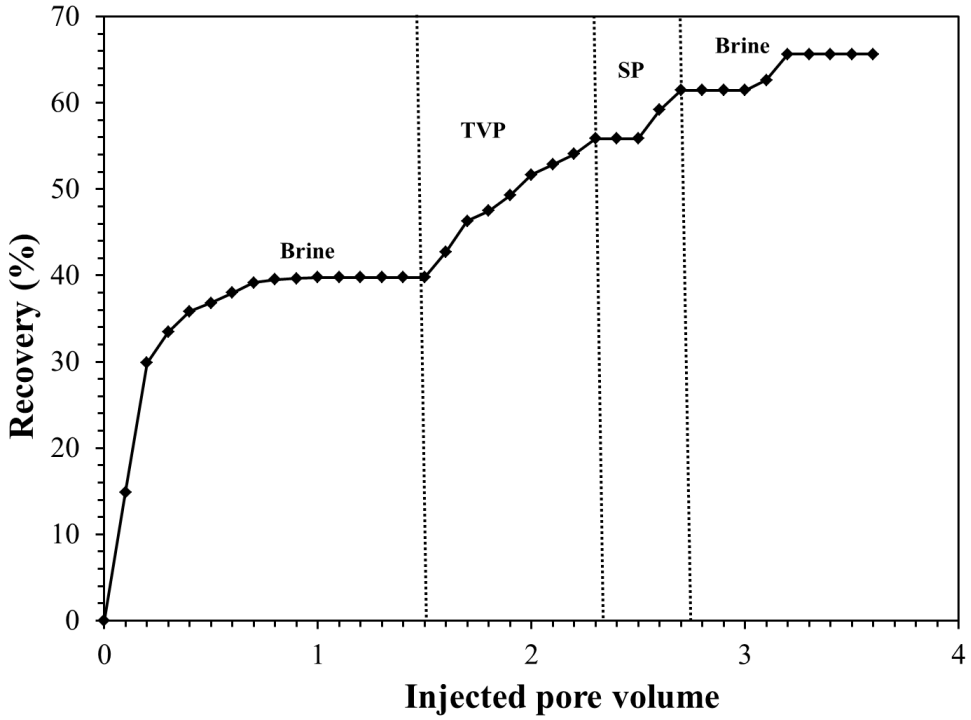

Figure 5-13: Oil recovery using 0.25% TVP and SP system consisting of 0.25% TVP and 0.05% surfactant

5.4 Conclusions

The thermo viscosifying polymer showed promising results desired for high temperature high salinity EOR applications. In the presence of salts, thermo-thickening behavior was observed for the polymer and the SP system. Thermo-thickening behavior was found to be dependent on the polymer concentration, salinity and temperature. At low salinity, only thermo-thinning behavior was observed for the entire temperature range covered in this study. At high salinity, the thermo-thinning was observed at low temperatures followed by thermo-thickening at high temperatures. Critical temperature decreased from 64^{o}C to 51^{o}C upon increasing the polymer concentration from 0.3 to 1.0%. The SP system also showed thermo-thickening behavior and similar dependency on temperature and salinity was obtained. Addition of the surfactant caused increase in the viscosity at low temperatures (<80^{o}C), while at high temperatures (>80^{o}C) the viscosity of the SP system is almost independent of the surfactant concentration. The fluorocarbon surfactant in combination with the co-surfactant was able to reduce the IFT from 10 to 10^{-2}mN/m. From core flooding, 22% additional oil recovery was achieved using the SP system. Viscosity built-up due to thermo-thickening is promising for EOR applications in HTHS reservoirs and better mobility ratio can be achieved at hostile conditions. However, the molecular weight of the TVP needs to increase so that high viscosity can be achieved at low polymer concentrations.

5.5 Acknowledgements

This research is supported by Saudi Armco through Project No CPM 2297. Authors would like to thanks Center of Petroleum and Minerals, King Fahd University of Petroleum & Minerals and Saudi Armco for financial support. Authors would like to thank SNF for providing polymer samples.

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CHAPTER 6

SCREENING OF AMPHOTERIC AND ANIONIC SURFACTANTS FOR cEOR APPLICATIONS USING a NOVEL APPROACH

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Abstract

Surfactants are used in chemical enhanced oil recovery (cEOR) to increase the capillary number by decreasing the oil/water interfacial tension (IFT). In this work, carboxyl betaine based amphoteric and propoxylated anionic surfactants were evaluated for potential application in cEOR. Thermal stability of the surfactants was assessed using a novel approach based on FTIR, NMR and TGA analyses. The anionic surfactant showed lower initial IFT compared to the amphoteric surfactant. After aging at 90^{o}C for a period of 10 days, the amphoteric surfactant maintained its IFT, while almost two orders of magnitude increase in the IFT of the anionic surfactant was observed. TGA analysis showed that the two surfactants were thermally stable for short exposure times. For long term stability, both FTIR and NMR analyses showed structural changes in the aliphatic region after aging in the anionic surfactant. The thermally stable amphoteric surfactant was further evaluated at different concentrations, temperatures and salinity. By increasing the surfactant concentration, IFT decreased initially and then increased with the increase in surfactant concentration. The oil /water IFT decreased by adding salts and increased with the increase in temperature. The results of NMR, FTIR and TGA techniques showed good correlation with IFT measurements and showed the potential of using these techniques in screening surfactant.

Keywords: Surfactant; Chemical enhanced oil recovery; Reservoir; Interfacial tension; Stability

6.1 Introduction

In petroleum industry it is well known that only one third of the oil present in the known reservoirs is recoverable by economical primary recovery methods (Hirasaki, Miller et al. 2011). Chemical enhanced oil recovery (cEOR) is one of the techniques employed to oil reservoirs to recover the remaining oil which cannot be recovered by primary recovery. A number of chemical flooding methods were reported in the literature, such as surfactant (Aoudia, Al-Maamari et al. 2010; Alagic, Spildo et al. 2011), polymer (Seright 2010), alkali(Bortolotti, Macini et al. 2009), surfactant/polymer (Gong, Xu et al. 2008; Zhenquan, Aimei et al. 2012; Kamal, Hussien et al. 2013; Kamal, Sultan et al. 2014) and alkali/surfactant/polymer(Mandal and Ojha 2008; Zhu, Hou et al. 2012). Chemical methods are utilized to increase the viscosity of displacing fluid for better mobility control, to increase the sweep efficiency and to reduce the interfacial tension (IFT) between water and crude oil. Polymers are used to increase the viscosity of displacing fluid and to improve the mobility ratio, which helps in increasing the microscopic and macroscopic sweep efficiency (Wang, Xia et al. 2001; Xia, Ju et al. 2004; Xia, Wang et al. 2004; Xia, Wang et al. 2007; Kuru 2010; Yu, Jiang et al. 2010).Alkalis reduce the adsorption and generate in situ surfactant by reacting with the acidic components of crude oil. Surfactants can mobilize residual oil by altering wettability and generating ultra-low IFT between crude oil and water (Samanta, Ojha et al. 2011). The ultra-low IFT is necessary to increase the capillary number and to overcome capillary forces (Barnes, Smit et al. 2008).Capillary number is a dimensionless group directly related to oil recovery and defined as the ratio of viscous forces to interfacial forces acting on the oil drop. A decrease in IFT from 20 to 10^{-2}mN/m can increase the capillary number to three orders of magnitude (Liu, Dong et al. 2004; Wu, Iglauer et al. 2010).

Ultra-low IFT is only one requirement and can be obtained with various commercial surfactants. However, for high incremental oil recovery the surfactant must be compatible with reservoir brine, thermally stable and have low adsorption on reservoir rock. Moreover, for economic reasons the surfactant must be cheap and commercially available in large quantities. A surfactant that is suitable for one reservoir is not necessarily suitable for other reservoirs due to the different nature of rock, crude oil temperature and water salinity. For example, carbonate rocks have positive charges on the surface and therefore anionic surfactants have very high retention on the rock surface. Due to the stringent requirements, surfactants are screened by series of screening steps. These may include: compatibility with sea water, phase behavior, IFT, adsorption and finally core flooding experiments.

In addition to the techniques reported in the literature to evaluate surfactants for cEOR applications, we proposed an alternative modified approach based on the structural analysis of the surfactants. In this approach, the compatible surfactants were evaluated for short term thermal stability using TGA followed by long term thermal stability test using NMR and FTIR analyses before and after exposure at the desired conditions. Finally, IFT results before and after aging were related to NMR and FTIR results. This approach can be helpful in identifying those surfactants having low IFT at unexposed conditions, but gain high IFT after exposure.

In this work, thermal stability of carboxyl betaine based amphoteric surfactant (surfactant-A) and anionic surfactant (surfactant-B) was evaluated. A comparison was also made between IFT of both surfactants before and after aging. The IFT of the

thermally stable surfactant-A was further investigated at different concentrations, salinity and temperatures.

6.2 Experimental

6.2.1 Materials

Carboxyl betaine based amphoteric surfactant (surfactant-A) supplied by Oil Chem Technol., USA. Surfactant-B is propoxylated anionic surfactant with trade name AlfoterraL167-4ssupplied by Sasol® North America Inc. The structure of surfactant-B is shown in Figure 6-1. Synthetic sea water (SW) was prepared using laboratory grade sodium bicarbonate, sodium sulphate, sodium chloride, calcium chloride and magnesium chloride with a total salinity of 57,643 mg/L (ppm). Composition of synthetic SW is given in Table 6-1. Dead oil used in interfacial tension experiments, was of Othmaniyah reservoir having a density of 0.8725 g/cm^3 and a viscosity of 13.1 cP

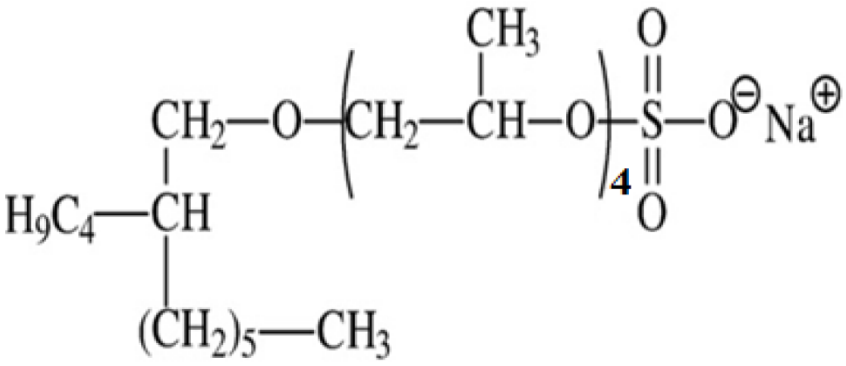

Figure 6-1: Structure of surfactant

Table 6-1: *Composition of SW*

Ions	Concentration (mg/L)
Sodium	18,300
Calcium	650
Magnesium	2,083
Sulfate	4,290
Chloride	32,200
Bicarbonate	120
TDS	57,643

6.2.2 Characterization

The IFT between water and crude oil was measured using spinning drop tensiometer supplied by Kruss. Thermogravimetric analysis (TGA) was carried out using SDT Q600 (TA instruments) under a nitrogen atmosphere at a heating rate of 10^{o}C/m from 25 to 500^{o}C. FTIR analysis of the surfactant samples was conducted in Nicolet 6700 spectrometer. NMR sample was prepared by transferring around 100 mg of the surfactant to 5 mm NMR tubes. 600 µl of D_2O was added to the NMR tube. NMR spectra were acquired on a JEOL 500 MHz spectrometer equipped with multinuclear probe. Thermal aging of the surfactant / SW solution was carried out at 90^{o}C for 10 days.

6.3 Results & Discussion

Thermal stability of the surfactants was evaluated using TGA, NMR and FTIR analyses. TGA analysis was carried out to determine the short term thermal stability of the surfactants. The objective of the TGA analysis was to screen out the surfactants which were not thermally stable for a short period of time. Surfactants unstable for the short term at the desired temperature (90^oC) need not to be evaluated for long term stability. From Figure 6-2 it can be observed that no major thermal loss was observed up to 90^oC for both surfactants. Weight loss at 90^oC was less than 1.5%. This weight loss may be due to some residual solvent. Major thermal events start after 130^oC. Due to good short term stability at the desired temperature (90^oC), both surfactants were further evaluated for long term stability using FTIR and NMR analyses.

FTIR spectra of surfactant-A and surfactant-B are shown in Figure 6-3 and Figure 6-4, respectively. Similar FTIR spectra for aged and non-aged samples of surfactant-A were recorded and there was no indication of any structural changes after aging of surfactant-A. However, a structural difference between aged and non-aged samples of surfactant-B is evident from Figure 6-4. A number of peaks in the region of 500-1600 cm^{-1} disappeared in the aged surfactant spectrum which indicates the changes in the structure of surfactant-B after aging. NMR analysis was performed to investigate further structural changes. ^{13}C-NMR of surfactant-B before and after aging is shown in Figure 6-5. Several different peaks can be observed from ^{13}C-NMR spectra of surfactant-B before aging. Downfield chemical shifts refer to the hydrocarbon chain and upfield chemical shifts refer to the carbon directly connected with the oxygen of propoxy groups. After aging, we did not observe any peak in the range of 20-35 ppm, while before aging several peaks

were present in this range. All the peaks between 20-35 pm correspond to aliphatic hydrocarbon chain and it was concluded that possible structural changes occurred in the aliphatic region. It was further supported by ^{1}H-NMR analysis.^{1}H-NMR spectra of surfactant-B before and after aging is shown in Figure 6-6. Downfield chemical shift in the range of 0.75-1.5 ppm is for hydrogen associated with aliphatic hydrocarbon chain and upfield chemical shift in the range of 3-3.5 refers to hydrogen associated with propoxy group. After aging, fewer peaks were observed in the lower range, which indicate possible structural changes in the aliphatic region and support ^{13}C-NMR observations.^{13}C-NMRspectra of surfactant-A is shown in Figure 6-7. Surfactant-A is carboxyl betaine based amphoteric surfactant with ethylene glycol butyl ether as a solvent. The chemical shift present in ^{13}C-NMR spectra refers to both solvent and surfactant.^{13}C-NMR spectra of surfactant-A clearly validates the surfactant thermal stability as no major structural changes were observed after aging. ^{1}H-NMR spectra shown in the Figure 6-8 also supports this finding and similar peaks were observed in ^{1}H-NMR spectra of surfactant-A before and after aging.

In summary, TGA analysis showed that both surfactants have short term thermal stability at 90^{o}C. FTIR and NMR analysis showed that surfactant-A was not stable at 90^{o}C when aged for 10 days and structural changes were observed in the aliphatic region. While surfactant-B was found to be thermally stable at the same temperature and for the same aging period. To relate IFT with these structural changes, IFT of aged and non-aged-solutions was determined at various temperatures. Figure 6-9 shows a comparison of both surfactants before and after aging. Surfactant-B has almost similar IFT before and after aging and no change in the IFT was observed. While, almost two orders of magnitude increase in the IFT of surfactant-A was observed after aging. This enormous increase in

the IFT is due to structural changes in surfactant-A after aging. Stable IFT value with aging is due to the thermal stability of surfactant-B. Most of the reported data of IFT in literature were obtained without any aging which may be misleading. To obtain more realistic IFT values, IFT should also be measured after exposure of surfactants to reservoir conditions. If a surfactant is found to be structurally stable at reservoir conditions, it will maintain the IFT. Before measuring the IFT, it is suggested that thermal analysis of surfactants should be carried out using a combination of FTIR and NMR techniques before and after exposing at the desired conditions. This approach helps with the fast identification of thermally stable surfactants among a large number of surfactants. However, to reach an optimum formulation adsorption and core flooding data must be considered.

Surfactant-A was further evaluated for thermal stability at 90^{o}C. The IFT between crude oil and saline water was measured at different temperatures and surfactant concentrations. Dynamic IFT was observed at all surfactant concentrations for both deionized water and sea water. Representative IFT vs. time plot is shown for surfactant-A in Figure 6-10 at 0.1 % concentration. Transient minimum IFT (0.0109 mN/m) was observed after 62 second. It's worth mentioning here that first reported data point of IFT is at least 2 minutes after the oil/ water contact. These 2 minutes were consumed in placing the oil drop in the spinning tube. The IFT continuously increased with time until it achieved an equilibrium value. This equilibrium IFT value is reported for all formulations at various conditions. The dynamic IFT behavior of some surfactants has been reported in many previous studies (Clint, Neustadter et al. 1984; Taylor, Hawkins et al. 1990; Taylor and Nasr-El-Din 1996; Zhao, Li et al. 2005; Aoudia, Al-Shibli et al. 2006; Aoudia, Al-Maamari et al. 2010).

Surfactant concentration is the most critical parameter and needs to be optimized for better recovery. IFT data for both deionized water and SW is shown in Figure 6-11. At all investigated concentrations, the IFT is lower for SW in comparison with deionized water. The addition of the surfactant decreased the IFT byabout2 orders of magnitude. A minimum equilibrium IFT was found to be at a surfactant concentration of 0.025% as shown in Figure 6-12. Further addition of the surfactant increased the IFT and maximum IFT was observed at 0.1 % surfactant concentration. This type of behavior was reported previously for other surfactant systems (Li, Mu et al. 2000; Wanli, Yi et al. 2000; Daoshan, Shouliang et al. 2004; Bortolotti, Macini et al. 2009). This behavior is related to adsorption and desorption of surfactant at the oil / water interface. Surfactant concentration at which the rate of adsorption is equal to the rate of desorption will give the minimum IFT (Li, Mu et al. 2000). If the concentration is lower than the critical concentration, the rate of adsorption of the surfactant will be higher than the rate of desorption. At the critical concentration these rates become equal. Further increase in the concentration results in a higher desorption rate from the interface and higher IFT. Another possible explanation of this behavior can be related tothe critical micelle concentration as discussed by Bortolotti (Bortolotti, Macini et al. 2009). At low surfactant concentration surfactant molecules remain in monomer form. Increase in concentration will increase the number of monomers in the solution. The maximum number of monomers and the minimum IFT exist at the critical micelle concentration (CMC). As the surfactant concentration increases, micelle formation starts and the number of monomer decreases. This micelle formation results in an increase in the IFT. The decrease in the IFT after 0.1 % is due to the formation of stable emulsions. For practical applications, optimum concentration (0.025%) is very small and surfactant loss

due to adsorption and phase trapping can decrease the concentration of the surfactant in flooding liquids.

The IFT between crude oil and SW at various surfactant concentrations and temperature is shown in Figure 6-12. For all investigated surfactant concentrations, IFT gradually increased with increasing temperature from 30^{o}C to 70^{o}C. Different observations were reported on the effect of temperature on IFT. Aoudia et al.(Aoudia, Al-Maamari et al. 2010) reported an increase in the IFT with the increase in temperature. Wu et al.(Aoudia, Al-Shibli et al. 2006) observed a decrease in the IFT with temperature using Alfoterra surfactant for n-decane/water system. While, for some sulfonate surfactant a decrease in the IFT was observed only up to specific temperatures. Further increase in temperature raised the IFT. Composition and nature of crude oil also decide how temperature will influence the IFT. For aromatic oil, it was observed that temperature has no effect on the IFT up to 50^{o}C and further increase in temperature raised the IFT. For the same surfactant system, IFT decreased with temperature for naphthenic oil. While, paraffinic oil showed exactly opposite IFT-temperature behavior to that of aromatic oil(Aoudia, Al-Shibli et al. 2006).

Figure 6-13 shows the effect of adding salt on the crude oil/water IFT at 0.1 % surfactant concentration. Deionized water has the highest IFT which decreased by adding salts. Salinity has a significant effect on interfacial properties. At low concentration of salts, most surfactants dissolve in aqueous phase while at high salinity surfactant stay in oleic phase. However, at optimal salinity the surfactant equally dissolves in oil and aqueous phase and gives the least IFT (El-Batanoney, Abdel-Moghny et al. 1999; Li, Mu et al. 2000; Wang, Liu et al. 2010; Wu, Iglauer et al. 2010). For the investigated system, only a

decrease in the IFT with salinity was observed. It may be due to the fact that the maximum investigated salinity is 57,543 mg/L, and it is expected that further increase in salinity will increase the IFT after attaining a minimum. A similar observation was reported for Alfoterra 3n and 2n surfactant series (Wu, Iglauer et al. 2010) where up to 8% NaCl concentration only a decrease in the IFT was observed .

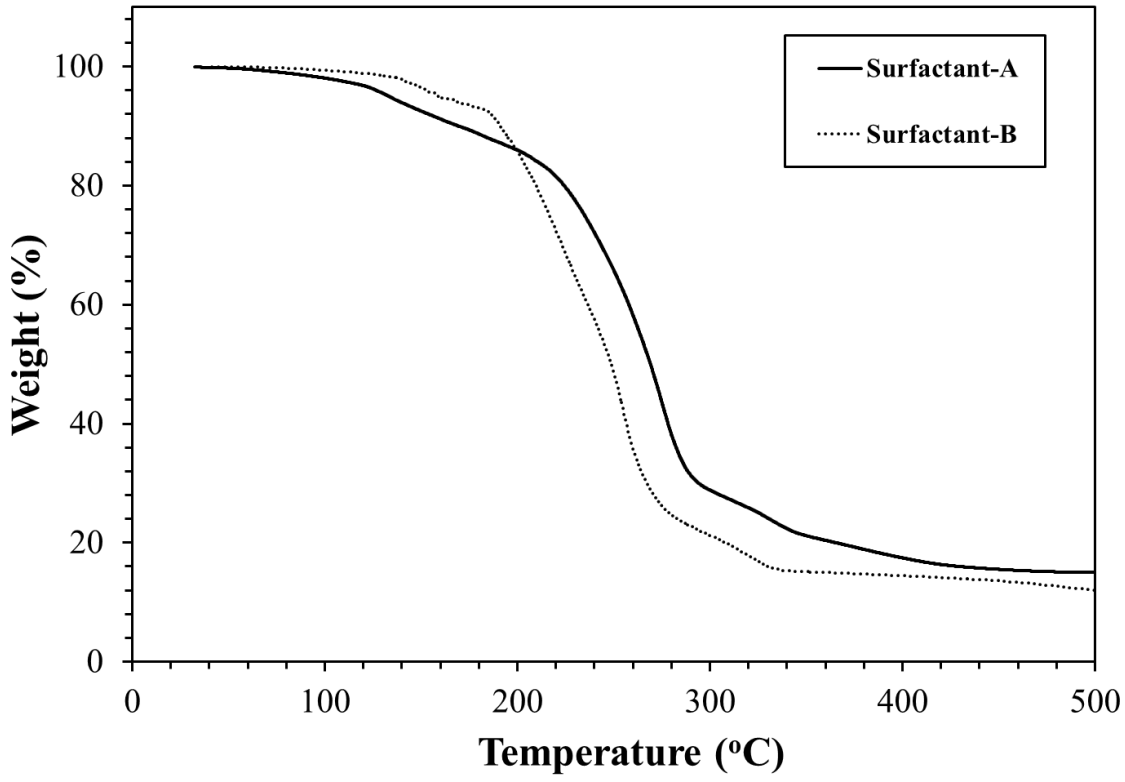

Figure 6-2: TGA curves of surfactants under nitrogen atmosphere

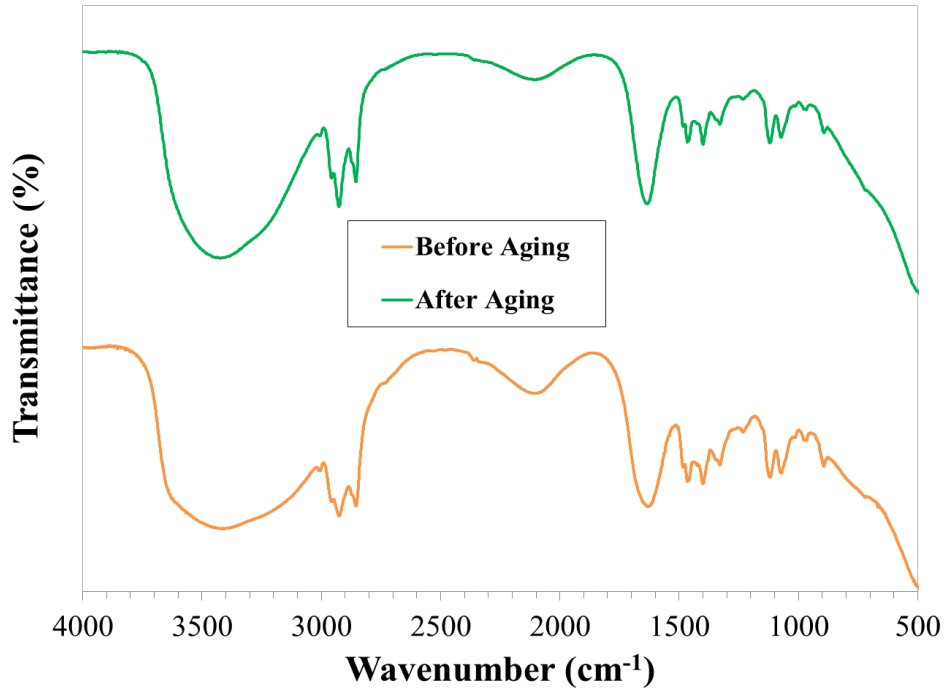

Figure 6-3: FTIR spectra of surfactant-A before and after aging

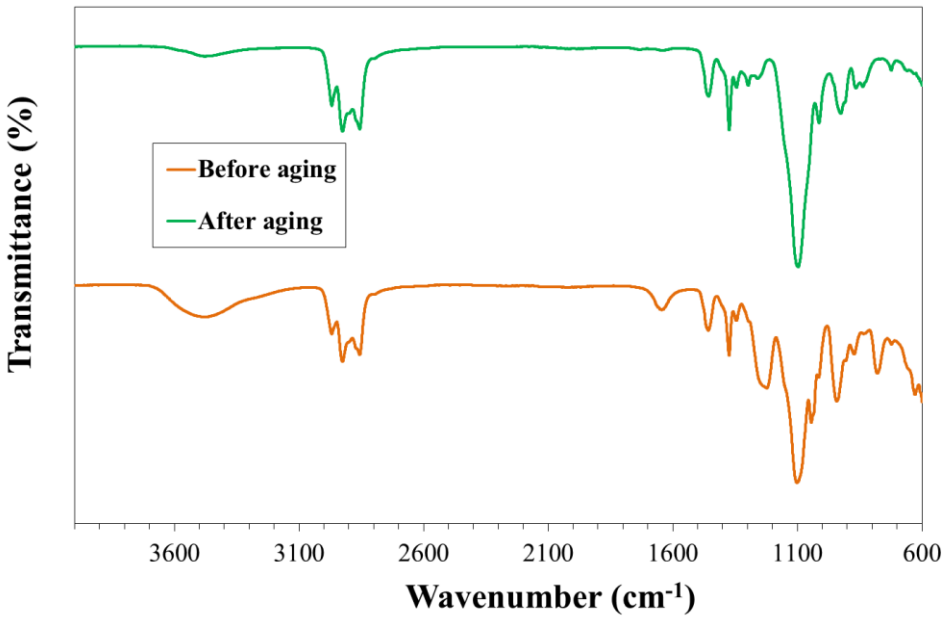

Figure 6-4: FTIR spectra of surfactant-B before and after aging

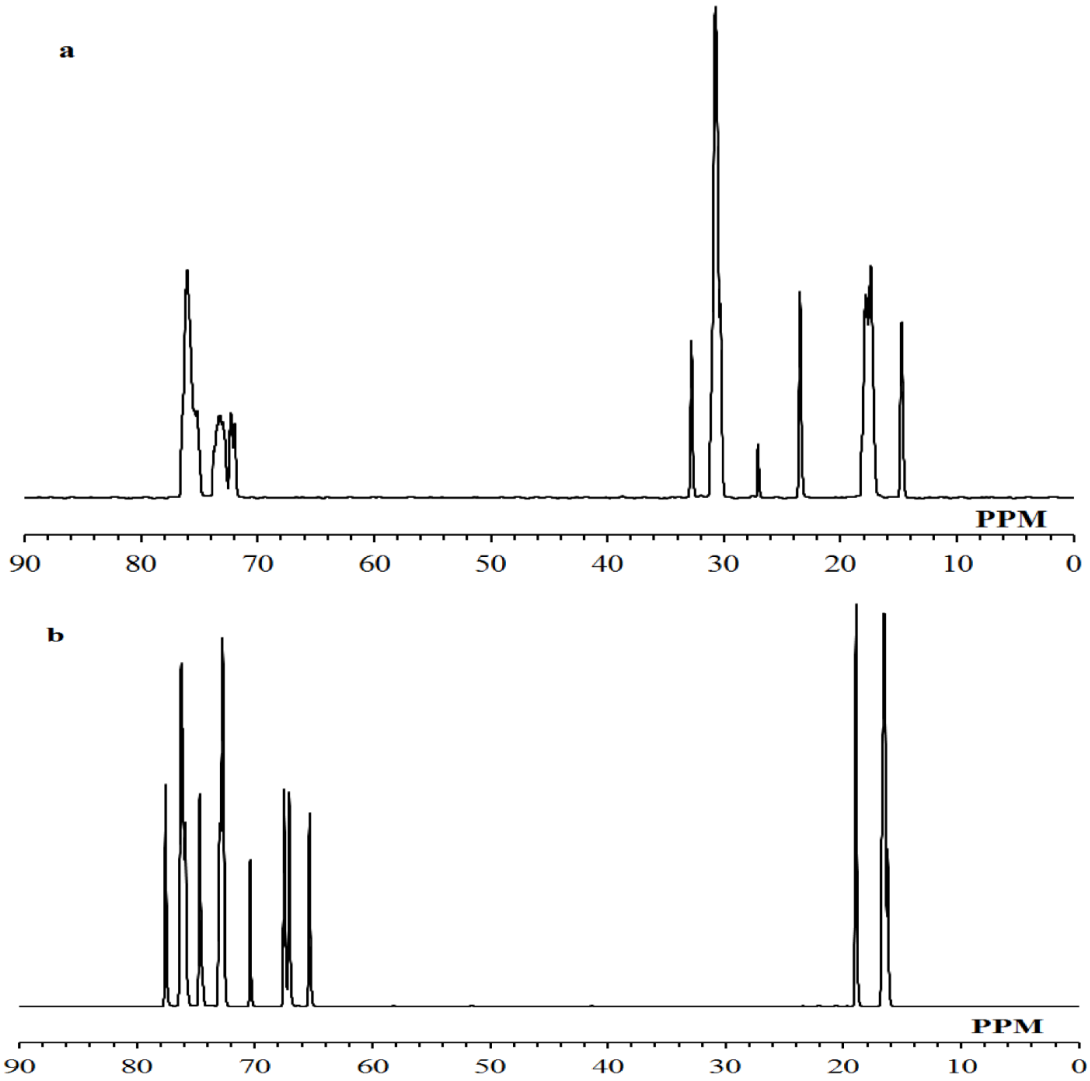

Figure 6-5: ^{13}C-NMR spectra of surfactant-B; a) before aging, b) after aging

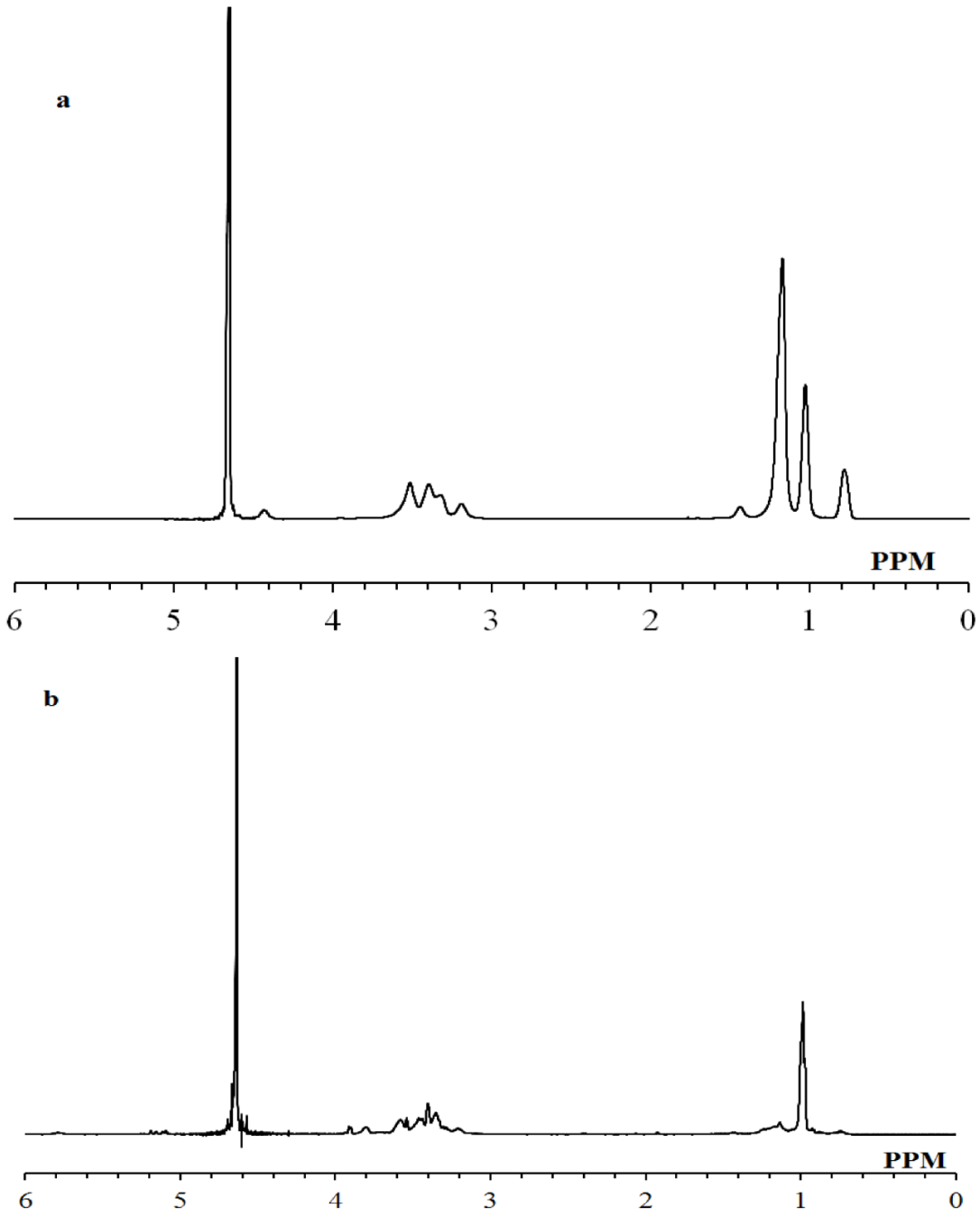

Figure 6-6: ^{1}H-NMR spectra of surfactant-B; a) before aging, b) after aging

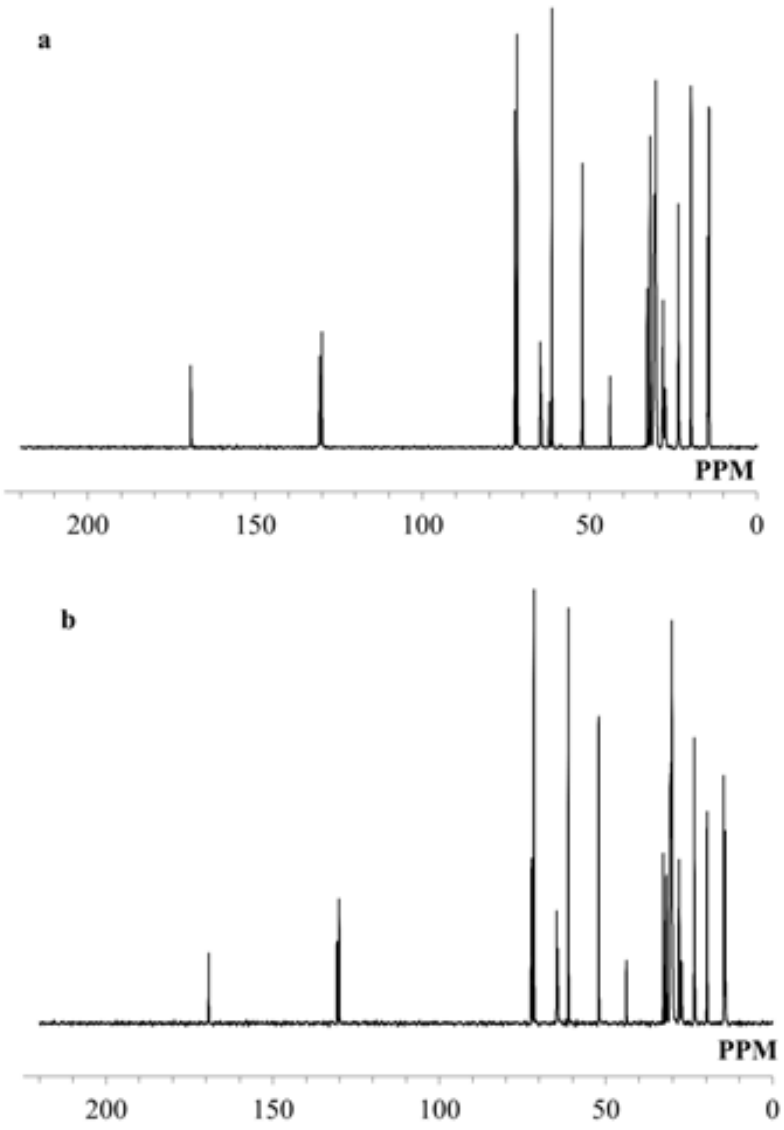

Figure 6-7: ^{13}C-NMR spectra of surfactant-A; a) before aging, b) after aging

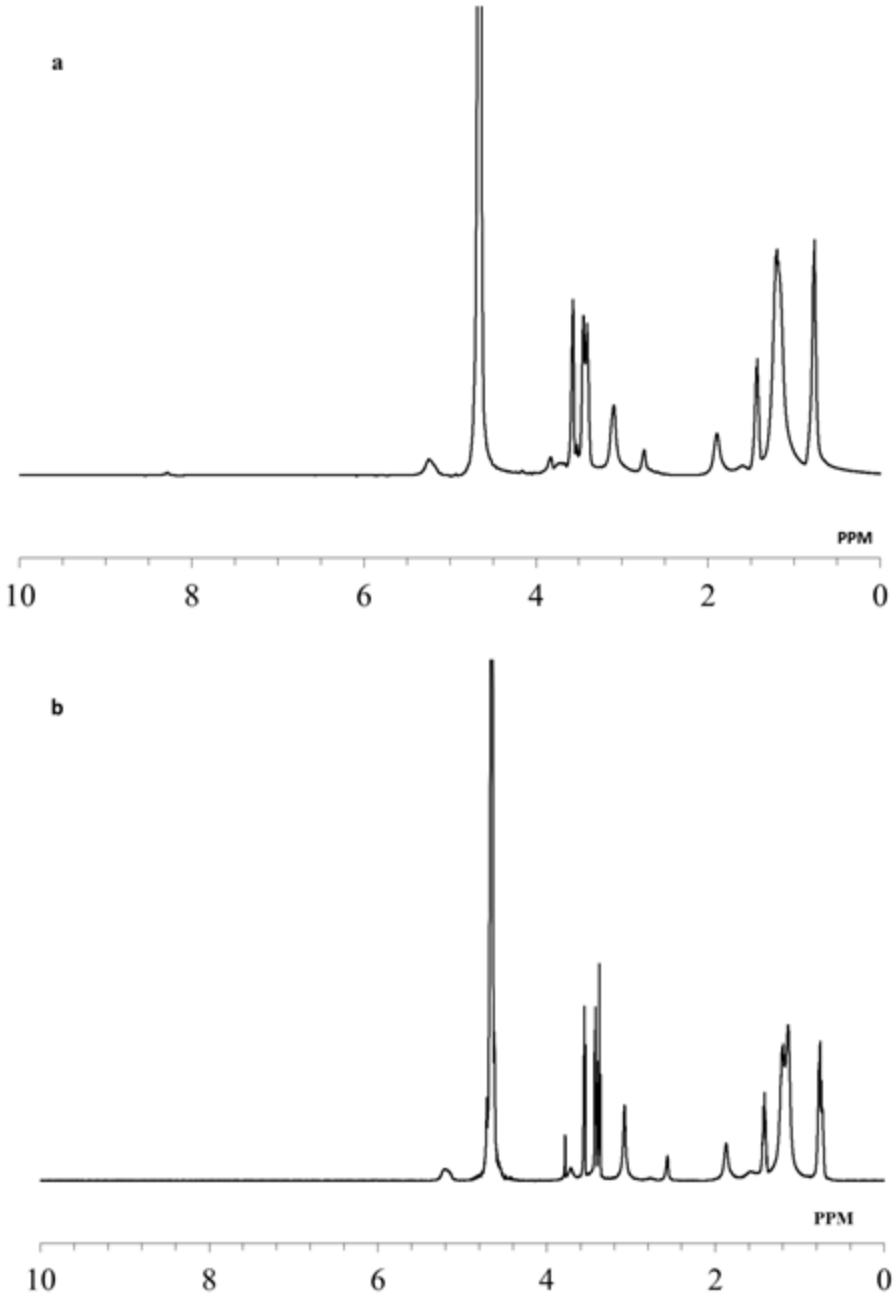

Figure 6-8: ^{1}H-NMR spectra of surfactant-A; a) before aging, b) after aging

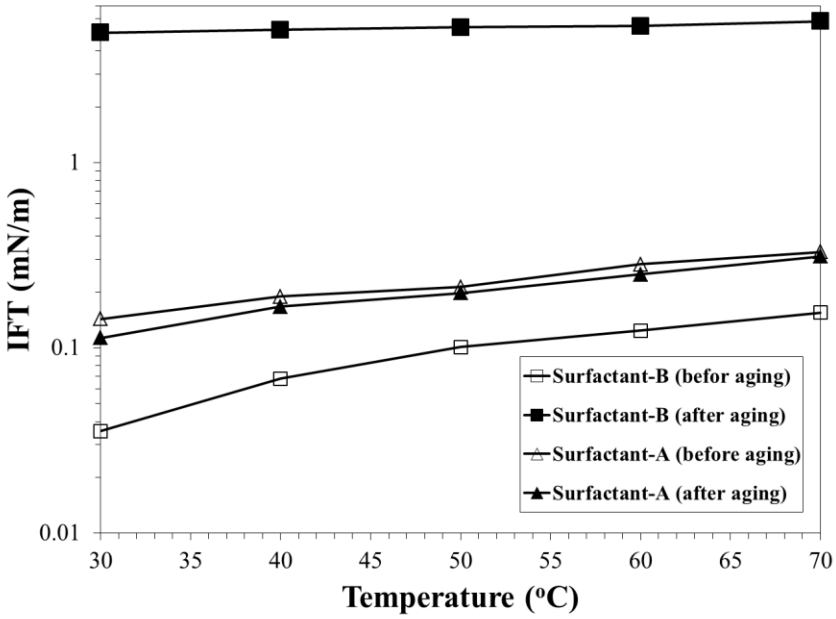

Figure 6-9: IFT Comparison of surfactants before and after aging

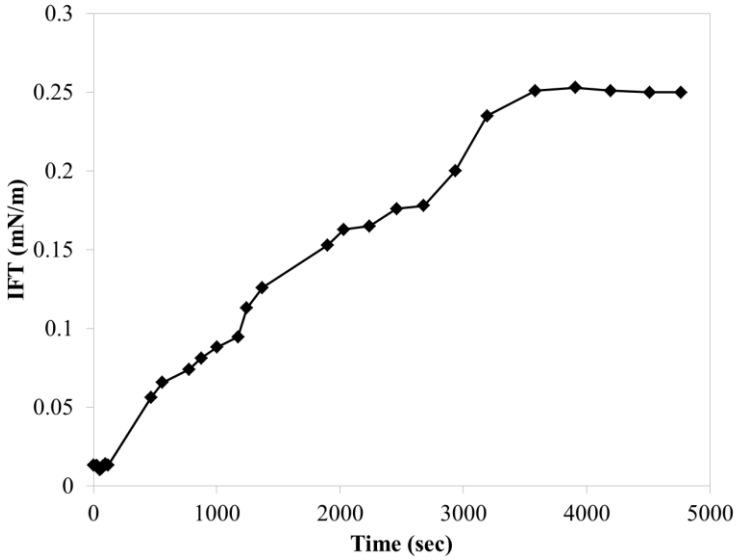

Figure 6-10: Variation of IFT between crude oil and SW at 0.1 % surfactant concentration with time at 30°C

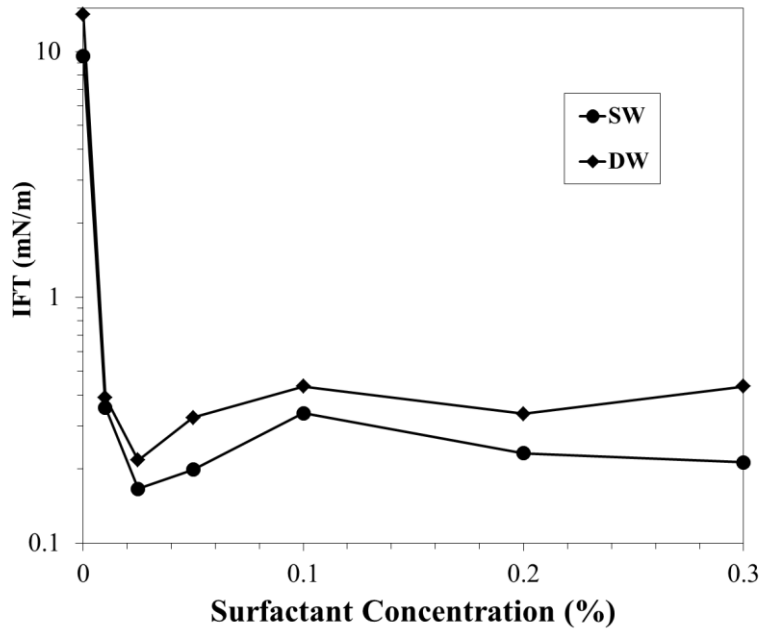

Figure 6-11: Effect of surfactant concentration on IFT between crude oil and SW at 50^{o}C

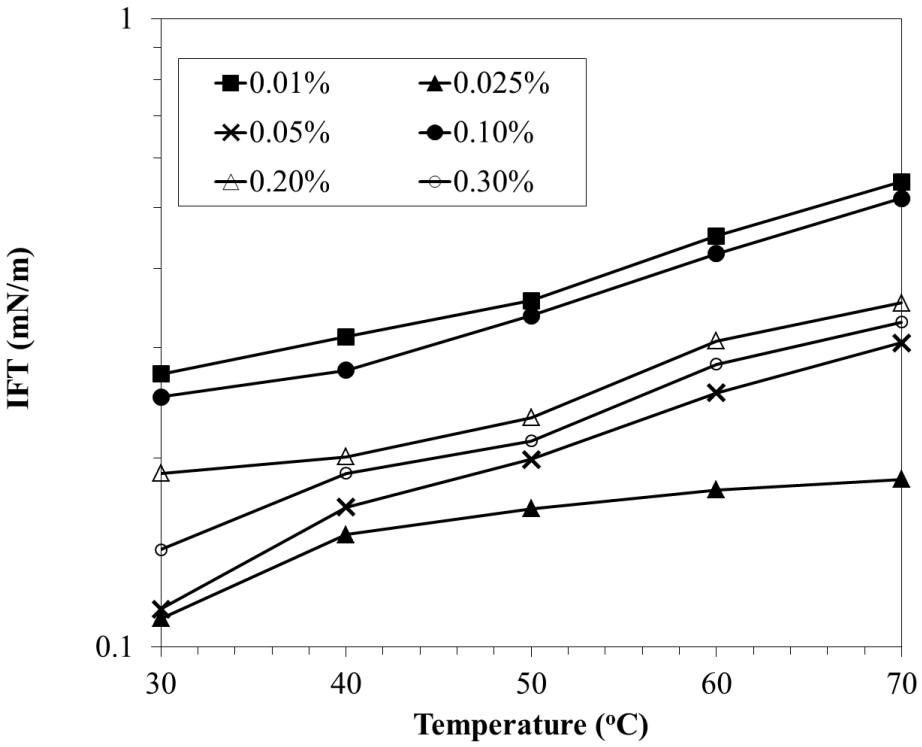

Figure 6-12: Effect of temperature on IFT at different surfactant concentration

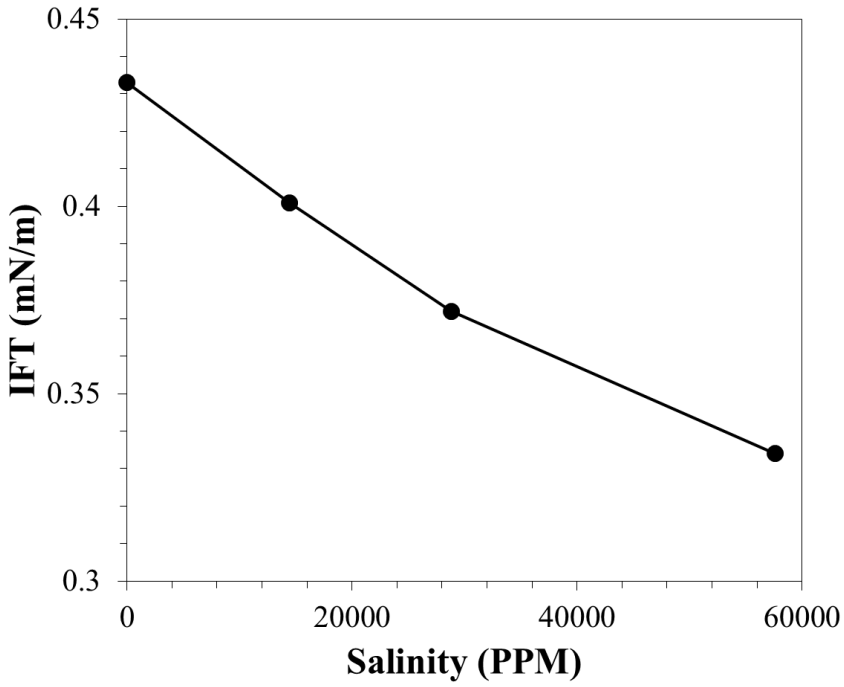

Figure 6-13: Effect of salinity on IFT at 0.1 % surfactant concentration at 50^{o}C

6.4 Conclusions

In this work, a novel approach based on IFT, thermal and structural analysis was adopted to identify the thermally stable surfactants used in cEOR applications. Short term thermal stability was assessed by TGA and possible structural changes after aging were identified using FTIR and NMR. IFT data were correlated with NMR and FTIR measurements before and after the exposure of the surfactants at the desired conditions. The approach was applied on two surfactants but can be generalized to screen surfactants for cEOR application. TGA data showed that carboxyl betaine based amphoteric surfactant (surfactant-A) and anionic surfactant Alfoterra L167-4s (surfactant-B) had no significant weight loss at 90^{o}C. However, NMR and FTIR data showed that surfactant-B was thermally unstable at 90^{o}C when aged for 10 days. While, surfactant-A was stable for the

same aging period and no structural changes were observed. After aging, two orders of magnitude increase in the IFT of surfactant-B were observed, although it has much lower initial IFT compared to surfactant-A. IFT of surfactant-A did not change significantly after aging. This approach can be helpful in identifying those surfactants having low IFT at unexposed conditions, but gain high IFT after exposure for a long time. Based on these results, it is recommended to examine the thermal stability of the surfactants before IFT measurements. Thermally stable surfactants identified by this approach can then pass through further screening tests. The thermally stable surfactant-A was further evaluated at different surfactant concentrations, salinity and temperatures. Two types of IFT were observed at all the investigated surfactant concentrations. Transient minimum IFT and equilibrium IFT were in the range of 10^{-2}mN/m and 10^{-1}mN/m, respectively. The IFT decreased initially and then increased with the increase in surfactant concentration. Minimum IFT was observed at 0.025% surfactant concentration. With the increase in temperature an increase in the IFT was detected within the investigated temperature range. Addition of salts reduced the oil/water IFT of the surfactant. However, the effect of temperature and salinity on oil/ water IFT in the presence of surfactant-A was not significant and all values were within the same order of magnitude.

6.5 Acknowledgements

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CHAPTER 7

MEASUREMENT OF INTERFACIAL TENSION BETWEEN OIL AND WATER IN PRESENCE AND ABSENCE OF SURFACTANT USING MOLECULAR SIMULATION

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Abstract

A mesoscale simulation technique dissipative particle dynamics (DPD) was used to model the oil water interfacial tension in presence and absence of surfactant. Different model compounds with varying number of hydrocarbon chain were selected which include: hexane, nonane, dodecane and pentadecane. Interfacial density, interfacial thickness and interfacial tension was investigated by varying the simulation time, no of molecules, chain branching and surfactant concentration. Well defined oil/water interface was observed. Interfacial tension increased with increasing simulation steps and finally achieves a plateau. By increasing hydrocarbon tail interfacial tension was found to be increased. Simulation results for oil water system were in good quantitative and qualitative agreement with experimental results. Sodium dodecyl sulphate surfactant was also simulated at oil water interface. Simulation results suggest decrease in interfacial tension by increasing surfactant molecule similar to experimental observations. DPD technique can be applied for ternary system of oil, water and surfactant with reasonable success.

Keywords: Simulation; Reservoir; Interfacial tension; Stability; Dissipative particle dynamics

7.1 Introduction

Surfactants adsorb at the interface between oil and water and lower the interfacial tension. Lowering of interfacial tension is desired in many industrial processes like surfactant enhanced oil recovery. Choosing efficient surfactant among a large number of natural and synthetic surfactant is time consuming and challenging task. Also, surfactant efficiency in lowering the interfacial depends on several factors like: surfactant concentration, tail length, branching, temperature, salinity, nature of oil and surfactant head group.

Interfacial tension measurements are dynamic in nature and significant time is required to achieve equilibrium. Moreover, standard deviation is very high particularly in those experiments which involve measurement of ultra-low interfacial tension using spinning drop techniques. Also it difficult to obtain concentration of the surfactant at interface as it requires expensive neutron scattering experiments (Rekvig, Kranenburg et al. 2003). An attractive alternate to identify distribution and adsorption of the surfactant at oil/water interface is molecular dynamic (MD) simulations. Surfactant efficiency at the interface has successfully identified using computer simulations in early 90's.

For complex fluids, MD simulation is challenging and expensive technique as it may involve millions of atoms and therefore, large numbers of simulation steps are required. One way to avoid this expensive technique is to replace specific group of atoms into single "bead" in such a way that it reproduce Newtonian mechanics. Coarse graining group of atoms into single bead replaces atomic interactions into bead-bead interactions. One such technique is dissipative particle dynamic (DPD) introduced by Hoogerbrugge and Koelman in 1992 to study the hydrodynamic behavior (Hoogerbrugge and Koelman

1992). In this technique, soft spheres are modeled and their motion is governed by some collision rules. The method has been used successfully to various physical and chemical problems(Groot 2003)

Fundamental objects in DPD are beads in the same way to atomistic modeling where atoms are fundamental entities. Beads are different than elements in the sense that there are no fixed set of beads types and they don't have any standard properties values. For each fluids bead types must be defined with appropriate values to proceed further with simulation.

7.2 Methods

The DPD model is composed of N number of beads that move in volume V. The system update after a fixed discrete time step (Δt). Time evolution of beads is governed by Newton's equation of motion which was initially set by Groot and Warren. Total force act between two particles i and j which are separated by a distance r_{ij} can be summarized by equation 1

$$f_i = \sum_{j \neq i} F_{ij}^C + F_{ij}^D + F_{ij}^R \qquad (1)$$

Where $F^C{}_{ij}$, $F^D{}_{ij}$, $F^R{}_{ij}$ are the conservative, dissipative and random forces, respectively and given by equation (2), (3) and (4) respectively.

$$F_{ij}^C = \begin{cases} -a_{ij}\left(1 - |r_{ij}|/R_c\right)\hat{\boldsymbol{r}}_{ij} & |r_{ij}| < R_c \\ 0 & |r_{ij}| \geq 0 \end{cases} \qquad (2)$$

$$F_{ij}^D = -1/2\,\sigma^2\omega\left(r_{ij}\right)^2/KT\,\hat{\boldsymbol{r}}_{ij}\left(v_{ij}\hat{\boldsymbol{r}}_{ij}\right) \qquad (3)$$

$$F_{ij}^R = \sigma\omega\left(r_{ij}\right)\hat{\boldsymbol{r}}_{ij}\,\zeta/\sqrt{\delta t} \qquad (4)$$

Conservative force derive from a soft potential and tries to capture the effects of the "pressure" between different particles and it will account for hydrophobic effect in DPD simulation of oil/water with added surfactant (Denham 2008). Conservative force is linear up to a cut of distance (R_c) between beads and zero beyond this distance. Here a_{ij} is interaction parameter between bead i and bead j. The second type of force is a friction force between the particles and describes the viscous resistance in a real fluid. This force tries to reduce velocity differences and momentum between dissipative particles. Finally, there is a stochastic random force and it provides an energy input into the system. Random force and dissipative force built a thermostat. Here v_{ij} is the velocity difference of the particles i and j and $\hat{\boldsymbol{r}}_{ij}$ is unit vector. σ is noise amplitude and ζ is a random variable between 0 and 1 and $\omega(r) = 1\text{-}r$ for $r < 0$ and $\omega = 0$ for $r > 0$

Time step (Δt) is one of the important simulation parameter and should be chosen as large as possible without affecting the model accuracy. Larger time steps results more movement of beads and fast simulations. However, temperature will not remain constant if time step becomes too large. Time step of 0.05 was chosen as only 1% temperature rise was reported using time step of 0.06 (Denham 2008). One water bead consists of three water molecules and one carbon bead consists of 3 carbon atoms. Volume of H_2O molecule at room temperature is 30 Å and therefore of water bead is 90 Å. Using density of 3 beads per unit volume length will be 6.46 Å ($270^{1/3}$). Density of 3 was chosen as it is minimum value for which DPD equation of state holds (Denham 2008). The anionic surfactant was modeled using 4 tail beads and one head bead. Repulsion parameter (a_{ii}) is the most important parameter in DPD simulations and model accuracy is mainly

dependent on the repulsion parameter. Like interaction parameters can be calculated as a_{ww}=78 $kT\ N/\rho$=78 (Model A). Groot and Warren (Groot and Warren 1997) derived another way to determine the like interaction parameters as a_{ww}=75 $kT\ /\rho$ (Model B) and for kT=1 and ρ=3 a will be 25. Repulsion parameter between beads particles of different bead types (a_{ij}) can be related to Flory-Huggins interaction parameter χ (Abe 1999)

$$a_{ij} = a_{ii} + 3.497\ \chi_{ij} \tag{5}$$

Flory-Huggins interaction parameters was calculated using molecular simulation technique

7.3 Results & Discussion

Figure 1 shows typical snapshot of a simulation box containing oil, water and surfactant beads. It is clear from the snapshot shown in Figure 7-1 that surfactant molecules are located at the interface and with the head group (blue) in the water and tail group (brown) in the oil. Also a clear separation between oil and water can be observed. Figure 7-2 shows typical density profile of hexane water system. Density profile also shows clear separation of oil and water. Moreover, interface thickness can also be measured from simulated data which is difficult to obtain experimentally. Figure 7-3 shows mean diffusivity of hexane and water beads. This data is useful to have comparison of diffusivity of different beads.

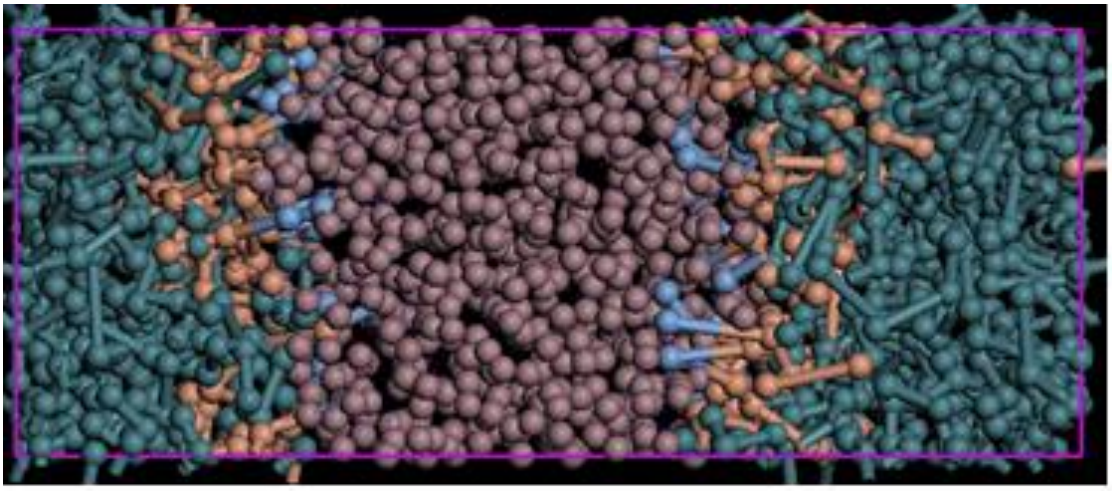

Figure 7-1: Typical snapshot of simulation box containing nonane, water and surfactant beads

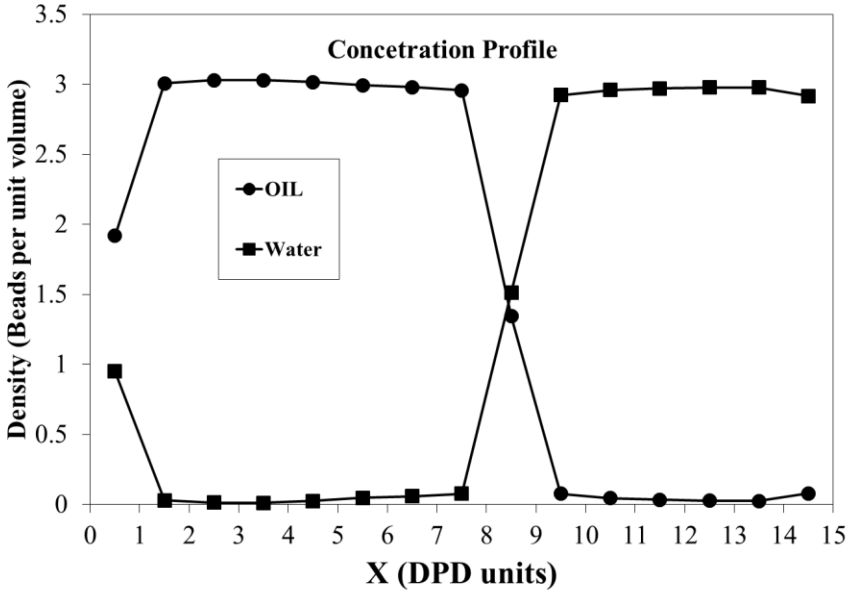

Figure 7-2: Typical density profile of hexane-water system

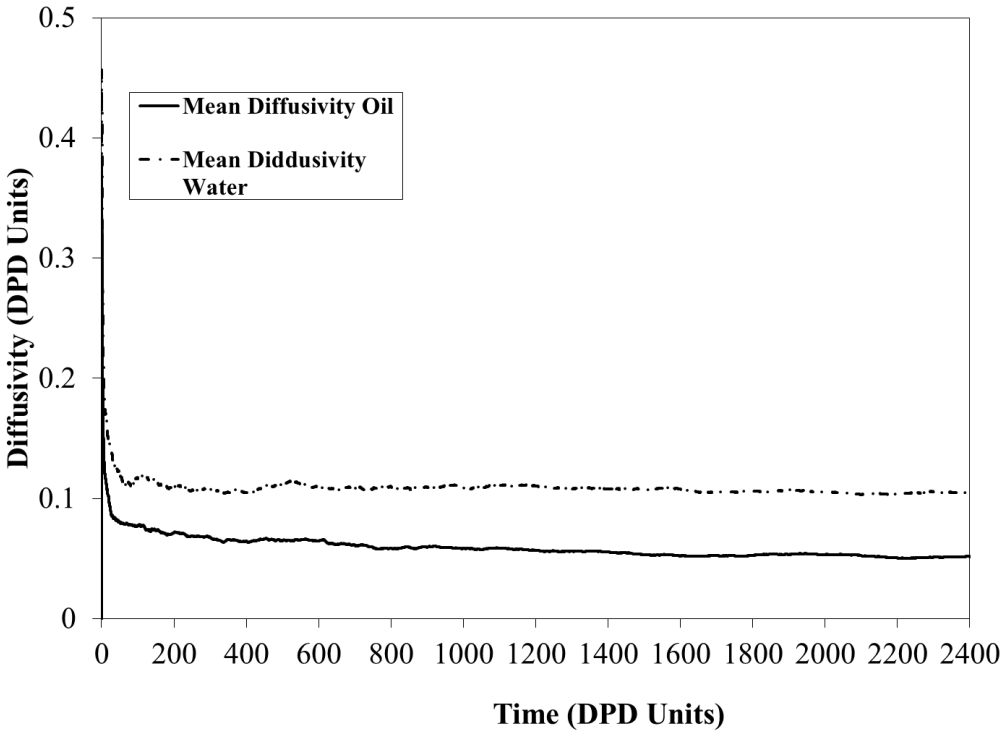

Figure 7-3: Typical simulated diffusivity data of hexane and water

Interfacial tension is a dynamic process and significant time is required to achieve equilibrium value. Therefore, significant numbers of simulation steps were used to reach an equilibrium value. Effect of number of simulation steps on IFT is shown in Figure 7-4. Equilibrium IFT was obtained after 50,000 steps. All further simulation was performed using 100,000 simulation steps. Also it is clear from Figure that pentadecane has highest IFT followed by dodecane and nonane. Hexane has lowest IFT obtained from simulations.

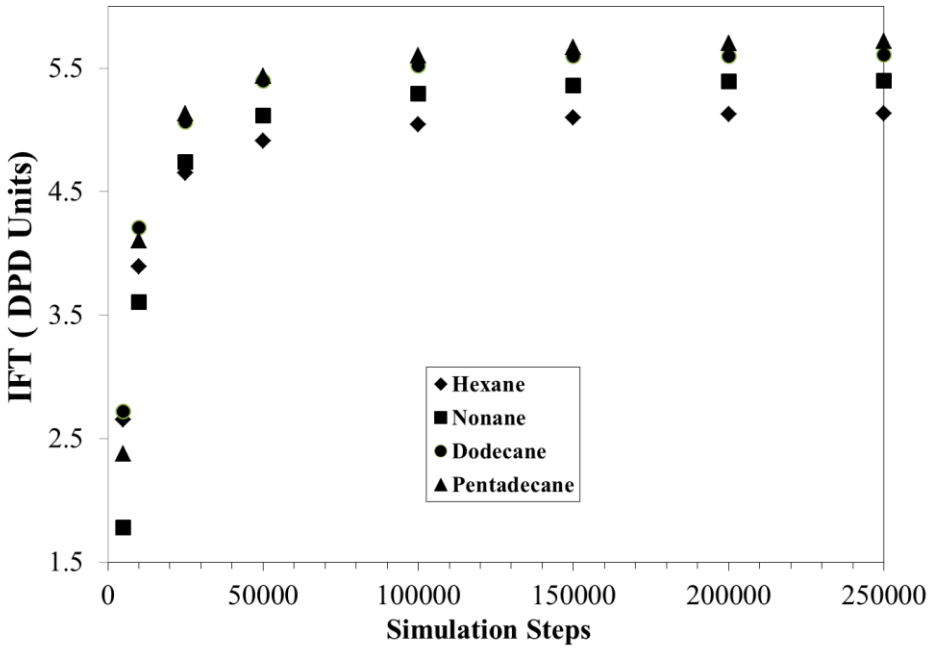

Figure 7-4: Effect of simulation steps on IFT of various hydrocarbons

Figure 7-5 shows a comparison of data obtained using model A and model B with experimental data. In model A like interaction parameters were calculated using a_{ww}=78 $kT\ N/\rho$=78, while in model B like interactions parameters were calculated using a_{ww}=75 $kT\ /\rho$. Both models gave good quantitative agreement with experimental data and similar trend was observed. However, model A gave results that were close to experimental values. Different results using two models are different types of parameterization. DPD results are strongly dependent on way of parameterization and bead repulsion parameters.

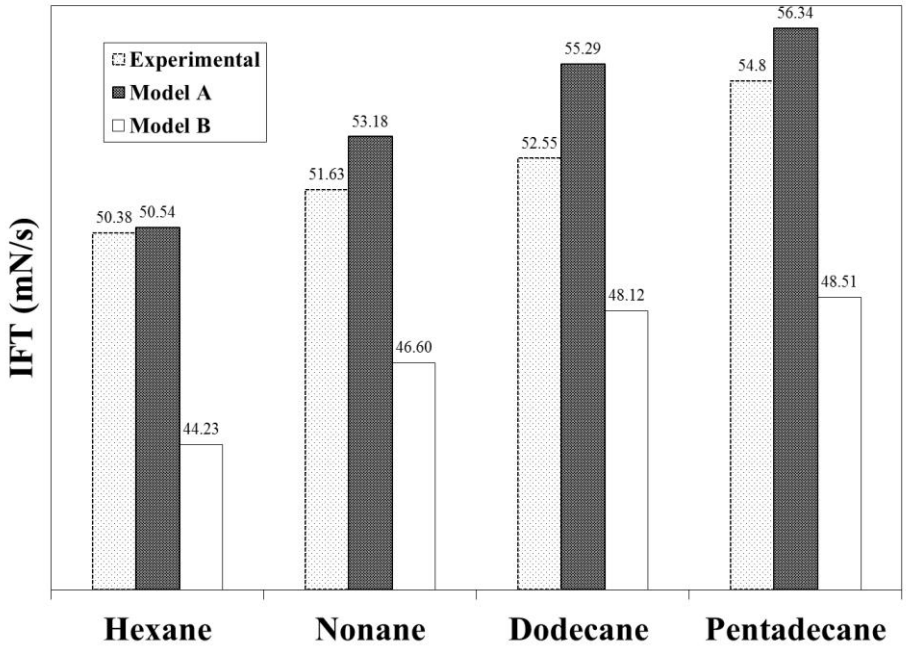

Figure 7-5: Comparison of simulated and experimental data

Figure 7-6 shows the effect of surfactant concentration on the oil/water IFT. Here different model oils were selected that include: hexane, nonane, dodecane and pentadecane. Adding more surfactant beads resulted in a decrease in the IFT for all investigated hydrocarbon. Increasing the chain length of hydrocarbon from hexane to pentadecane, increased the IFT which has been proved experimentally as well.

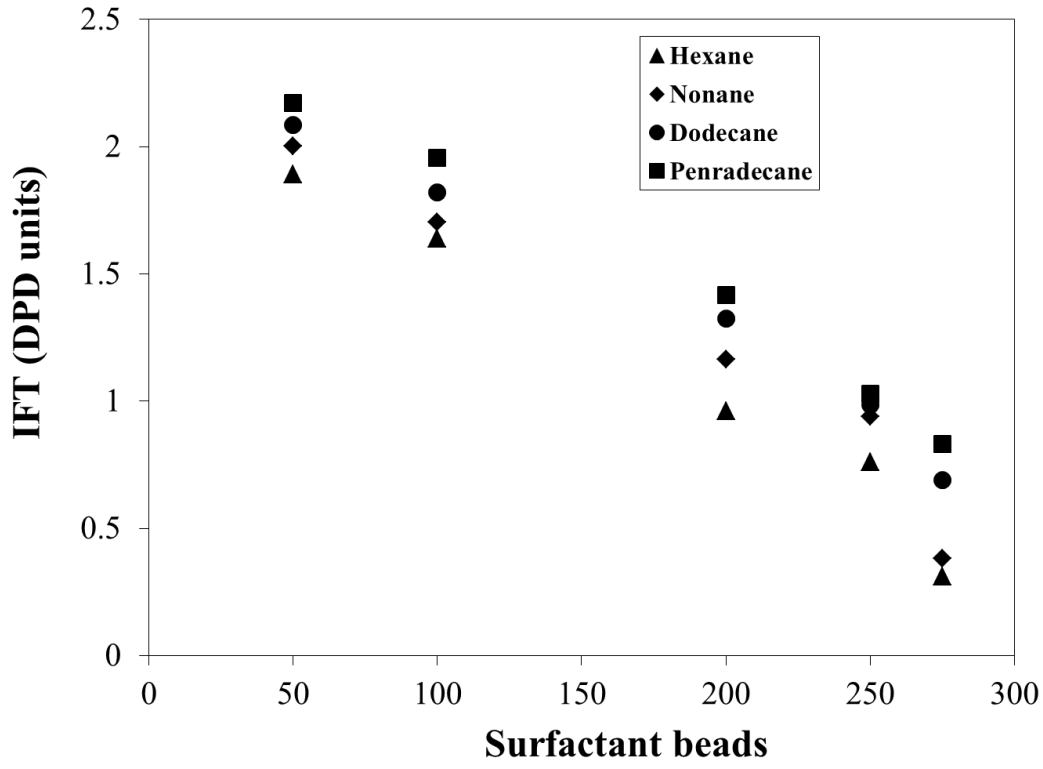

Figure 7-6: Effect of surfactant concentration on IFT

7.4 Conclusions

Different model compounds with varying number of hydrocarbon chain were evaluated using meso-scale simulation approach called dissipative particle dynamic (DPD). These model compounds include: hexane, nonane, dodecane and pentadecane. Interfacial density, interfacial thickness and interfacial tension was investigated by varying the simulation time, no of molecules, chain branching and surfactant concentration. Well defined oil/water interface was observed. Interfacial tension increased with increasing simulation steps and finally achieves a plateau. By increasing hydrocarbon tail interfacial tension was found to be increased. Simulation results for oil water system were in good quantitative and qualitative agreement with experimental results. Sodium dodecyl sulphate surfactant was also simulated at oil water interface. Simulation results suggest decrease in interfacial tension by increasing surfactant molecule similar to experimental observations.

7.5 Acknowledgements

This research is supported by Saudi Aramco through Project No CPM 2297. Authors would like to thanks Center of Petroleum and Minerals, King Fahd University of Petroleum & Minerals and Saudi Aramco for financial support.

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CHAPTER 8

CONCLUSIONS & RECOMMENDATIONS

In this work, the performance of various surfactant-polymer (SP) systems and their mutual interactions were investigated at high-temperature and high-salinity conditions. Different polymers and surfactants from different chemical classes were selected to develop a suitable SP system for carbonate reservoirs. Effect of polymer type and concentration, surfactant type and concentration, temperature, salt type and salt concentration on SP system was evaluated. Partially hydrolyzed polyacrylamide (HPAM) was not stable at high temperature (90^{o}C) and about 60% viscosity reduction was observed when temperature was increased from 50^{o}C to 90^{o}C. However, decrease in viscosity for copolymer of acrylamide (AM) and acrylamido tertiary butyl sulfonate (ATBS) copolymer was 15% for the same temperature range. The thermo viscosifying polymer showed promising results desired for EOR applications at high-temperature high-salinity conditions. In the presence of salts, thermo-thickening behavior was observed for the polymer and the SP system. Thermo-thickening behavior was found to be dependent on the polymer concentration, salinity and temperature. At low salinity, only thermo-thinning behavior was observed for the entire temperature range covered in this study. At high salinity, the thermo-thinning was observed at low temperatures followed by thermo-thickening at high temperatures. Critical temperature decreased from 64^{o}C to 51^{o}C upon increasing the polymer concentration from 0.3 to 1.0%. Viscosity

built-up due to thermo-thickening is promising for EOR applications in HTHS reservoirs and better mobility ratio can be achieved at hostile conditions.

The evaluated anionic surfactants were not compatible with typical field water and showed precipitation. The amphoteric and non-ionic surfactants showed high thermal stability and good compatibility with sea water and field water. A novel approach based on interfacial tension (IFT) measurements, thermal and structural analysis was adopted to identify the thermally stable surfactants. This approach is helpful in identifying those surfactants having low IFT at unexposed conditions, but gain high IFT after exposure for a long time. Short term thermal stability was assessed by TGA and possible structural changes after aging were identified using FTIR and NMR analyses. IFT data were correlated with NMR and FTIR measurements before and after the exposure of the surfactants at the desired conditions. The amphoteric surfactants were found to be most suitable due to their high thermal stability, lower adsorption and high efficiency to lower the interfacial tension between oil and water. The amphoteric fluorocarbon surfactant in combination with hydrocarbon amphoteric co-surfactant was able to reduce the IFT from 10 to 10^{-2}mN/m. Best SP system consisting of the thermoviscosifying polymer and the amphoteric surfactant was selected for the oil recovery experiment. From core flooding, 22% additional oil recovery was achieved using the SP system.

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University of Engineering & Technology,
Lahore Pakistan

AWARDS

- **Best PhD scholar** award for year 2013-2014 in Chemical Engineering
- **Best paper award** in Young Professional Technical Symposium, Dhahran, April 2013
- **Winner of 4th student conference paper competition** organized by Ministry of higher education, held in Makkah, Saudi Arabia, April-May, 2013
- Recipient of King Fahd University of Petroleum and Minerals Saudi Arabia scholarship from 2010 to 2014

MEMBERSHIPS

- Polymer processing society
- Society of petroleum engineers
- AICHE Saudi Arabian section
- Pakistan Engineering Council

INTERNSHIP & TRAINING

- DUPONT International, France (2 weeks)
- SPEL group of industries, Lahore Pakistan (4 weeks)
- Packages Private limited, Lahore Pakistan (4 weeks)

CO -SUPERVISION OF UNDERGRADUATE PROJECTS

- Synthesis and characterization of weather shield paint by varying the composition of binder and additives
- surface modification of polyethylene with methycrylic acid
- Production of methyl acetate via reactive distillation of methanol and acetic acid
- Plant design for production of Ammonia from coal gasification
- Production of high octane gasoline through HF alkylation

COMPUTER SKILLS

- MATLAB
- Aspen HYSYS
- Aspen Plus
- MS office
- Mathematica
- Material studio

RESEARCH EQUIPMENTS USED

- Discovery hybrid Rheomter
- Spinning drop tension meter
- Total organic carbon analysis (TOC)
- Thermal gravimetric analysis (TGA)
- Differential scanning calorimeter (DSC)
- Fourier transform infrared spectroscopy (FTIR)
- Crystallization analysis fractionation (CRYSTAF)
- Core flooding

LANGUAGE SKILLS

- English- Excellent oral and written skills
- Urdu –Excellent oral and written skills

JOURNAL PUBLICATIONS

1. Muhammad Shahzad Kamal, Abdullah S. Sultan, Usamah A. Al-Mubaiyedh, Ibnelwaleed A.Hussein, "Review on Polymer Flooding: Rheology, Adsorption, Stability and Field Applications of Various Polymer Systems", **Accepted, Polymer Review (I.F=6.5)**

2. Muhammad Shahzad Kamal, Abdullah S. Sultan, Usamah A. Al-Mubaiyedh, Ibnelwaleed A.Hussein, Yujun Feng, "Rheological Properties of Thermoviscosifying Polymer in High-Temperature and High-Salinity Environment", **In Press**

3. Muhammad Shahzad Kamal, Abdullah Saad Sultan, Usamah A. Al-Mubaiyedh, Ibnelwaleed A. Hussein, Martial Pabon, "Evaluation of Rheological and Thermal properties of a New Fluorocarbon Surfactant-Polymer System for EOR Applications in High-Temperature and High-Salinity Oil Reservoirs", Journal of surfactant and detergents, September 2014, Volume 17, Issue 5, pp 985-993

4. Muhammad Shahzad Kamal, Ibnelwaleed Ali Hussein, Abdullah Saad Sultan, Ming Han**,** "Rheological Study on ATBS-AM Copolymer-Surfactant System in High-Temperature and High-Salinity Environment," Journal of Chemistry, volume 2013.Article ID:801570

5. Muhammad Shahzad Kamal, Bijal Kottukkal Bahuleyan, Omer Bin Sohail, Abdul-Hamid M. Emwas, John E. Bercaw and Mamdouh A. Al-Harthi, "Crystallization analysis fractionation of poly(ethylene-co-styrene) produced by metallocene catalysts", Polymer Bulletin, 70, Issue 9 , pp 2645-2656

6. Muhammad Atiqullah, Mohammad M. Hossain, Muhammad Shahzad Kamal, Mamdouh Al-Harthi, Anwar Hossaen, Masiullaha J Khan and Ikram Hussain, "Crystallization kinetics of PE-*b*-*isotactic* PMMA diblock copolymer synthesized using $SiMe_2(Ind)ZrMe_2$ and MAO catalyst", AICHE Journal, 59(1) (2013) :200-214

7. Muhammad Shahzad Kamal, Abdullah S. Sultan, and Ibnelwaleed A. Hussein, "Evaluation of Amphoteric and Anionic Surfactants for cEOR Applications Using a Novel Approach" Submitted

8. Muhammad Shahzad Kamal, G. M. Mamoor, Nida Qamar, Muhammad farooq, S Muhammad, Free radical graft modification of polyethylene with methacrylic acid and styrene, Chemical Engineering Research Bulletin 15,(2011) 34-38

9. G. M. Mamoor, Nida Qamar, Umer Mehmood, Muhammad Shahzad Kamal, Effect of short glass fiber on mechanical and rheological properties of PMMA/SBR vulcanizates, Chemical Engineering Research Bulletin 13 (2009) 41-44

10. A.Ali, S.Shahid, N.Khan, N.Qamar, Muhammad Shahzad Kamal, Effect of treated wood flour on mechanical, rheological and water absorption properties of PS/UP reactive blend, Pakaistan Engineering Journal, 2009, May-August

11. G. M. Mamoor, Nida Qamar, Muhammad Shahzad Kamal, M.Z.Iqbal, Effect of untreated wood flour on mechanical, rheological and water absorption properties of ABS/SBR vulcanizates ,Pakistan Engineering Journal,2010, Jan-March

12. Muhammad Shahzad Kamal, Rizwan Khan, Irfan Wazeer, Zahid Maqbool, and Shahbaz Ahmad, Synthesis and characterization of weather shield paint by varying the composition of binder and additives (Engineering News, A Journal of Pakistan Engineering Congress, Vol. 15, 2010)

13. Umer Mehmood, Muhammad Shahzad Kamal, Nida Qammar and Muhammad Majid**,** Synthesis and characterization of two-component Acrylic based adhesive via free radical polymerization (Engineering News, A Journal of Pakistan Engineering Congress, Vol. 43, 2010)

CONFERENCE PAPER

1. Muhammad Shahzad Kamal, Ibnelwaleed A. Hussein, Abdullah S. Sultan, Usamah A. Al-Mubaiyedh**, "**Rheological study of a novel hydrophobically associating polyacrylamide-surfactant system for enhanced oil recovery", International conference of the polymer processing society, Cleveland, Ohio, USA, June, 2014.

2. Muhammad Shahzad Kamal, Abdullah S. Sultan, Ibnelwaleed A.Hussein, Ming Han, "Rheological Properties of Thermoviscosifying Polymers in High-Temperature High-Salinity Environment", AICHE annual meeting 2013, San Francisco, CA, USA, November 3 – November 8, 2013.

3. Muhammad Shahzad Kamal, Abdullah S. Sultan, Ibnelwaleed Ali Hussein, "Rheological Investigation of Interactions between Anionic Surfactant and Polyacrylamide for Chemical Flooding In Saudi Arabian Reservoirs", Fourth student conference, Makkah, Saudi Arabia,April-May,2013.

4. Muhammad Shahzad Kamal, Abdullah S. Sultan, Ibnelwaleed Ali Hussein, "Thermal Stability of fluorocarbon Surfactant and Interactions with polymers used For EOR", Young Professional Technical Symposium, Dhahran, April 2013.

5. Muhammad Shahzad Kamal, Abdullah S.Sultan, Ibnelwaleed Ali Hussein, "Review on Chemical EOR for high temperature/high salinity reservoir conditions", International EOR & Heavy Oil Conference, Muscat, Oman, March 2013.

6. Muhammad Shahzad Kamal, Abdullah S. Sultan, Usamah A. Al-Mubaiyedh, Ming Han and Ibnelwaleed A. Hussein, "Impact of salinity and temperature on

the rheology of partially hydrolyzed polyacrylamide solutions",28th International conference of the polymer processing society, Pattaya, Thailand, December 2012.

7. Muhammad Shahzad Kamal, "Effect of surfactant concentration, temperature and counterions on the rheological properties of polyacrylamide /surfactant system" SPE Middle East Sub Regional student paper contest Saudi Arabia sub regional heat, November, 2012.

8. Muhammad Shahzad Kamal, Mamdouh-Al-Harthi, "Styrene as a promoter, modifier and copolymer in ethylene polymerization", Third student conference, Al-Khobar, Saudi Arabia,April-May,2012.

9. M Atiqullaha , M,ohammad M. Hussain , Muhammad Shahzad Kamal, Mamdouh-Al-Harthi, Anwar hussain , Masiulla J Khan and Ikram Hussain, "Metallocene –catalyzed diblock copolymerization of methyl methacrylate with ethylene " ,21st Annual Saudi –Japan Symposium,Catalyst in Petroleum Refining and Petrochemicals,Dhahran , Saudi Arabia,November,2011.